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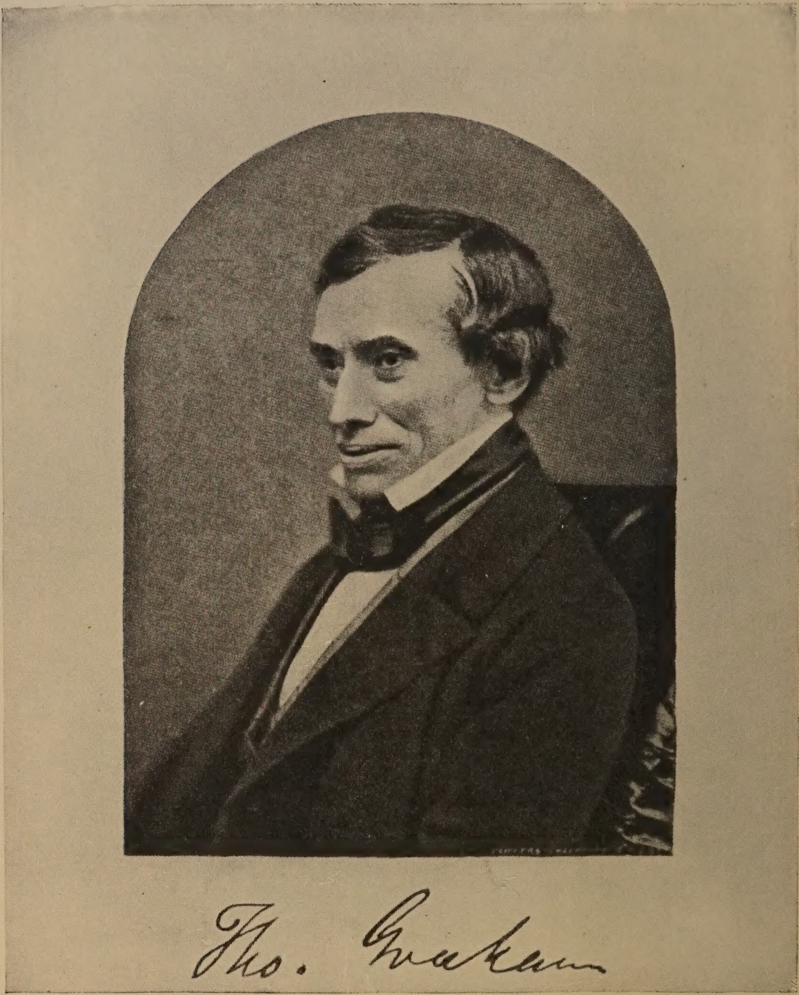

Tho. Graham

Frontispiece

THOMAS GRAHAM

AN INTRODUCTION TO

THEORETICAL AND APPLIED COLLOID CHEMISTRY

"THE WORLD OF NEGLECTED DIMENSIONS"

BY

DR. WOLFGANG OSTWALD

Professor in the University of Leipzig

AUTHORIZED TRANSLATION FROM THE EIGHTH GERMAN EDITION

BY

DR. MARTIN H. FISCHER

Eichberg Professor of Physiology in the University of Cincinnati

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TO

Dr. Martin H. Fischer

Professor of Physiology in the University of Cincinnati

IN SINCERE FRIENDSHIP

PREFACE TO THE SECOND AMERICAN AND EIGHTH GERMAN EDITIONS.

The editions preceding this have been exhausted in successively shorter periods — the last in a little more than six months. Such friendly reception touches my sense of responsibility. A thing so widely read needs to be tested and thought about. If the volume is to be more than a momentary cross-sectional view of colloid chemistry, if it is to continue in the eyes of a scientific world an introduction to the subject, repeated revision will be necessary. For this reason this edition has been gone over carefully, been improved and enlarged. I have previously emphasized the limits that must be set for enlargement and yet this volume contains some thirty additional pages. It seemed unnecessary to increase the number of demonstration experiments for I have collected many such in a laboratory manual.[1]

Let me emphasize again that this volume is not a substitute for, but only a stimulus to the seeing of colloid phenomena for oneself.

Wolfgang Ostwald.

Leipzig, *August,* 1922.

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[1] Wolfgang Ostwald, Kleines Praktikum der Kolloidchemie, Dresden, 1920.

PREFACE TO THE FIRST EDITION.

This small volume is the literary result of a series of lectures which I gave during the winter of 1913 and 1914 in the United States and Canada upon the invitation of a number of American universities. Originally invited by five universities, I found the interest in the science with which this volume deals so great that their number grew to sixteen while the actual number of lectures demanded of me during some seventy-four days was fifty-six. Lack of time and strength compelled me then to forego the pleasure of accepting further invitations. By way of expressing my thanks and my appreciation of the friendliness and the high honor of these invitations and in order to send greetings once more to my many scientific friends on the other side, I beg to list the universities and institutions in which it was my privilege to discuss colloid chemistry. They are the University of Cincinnati (where I spoke under the auspices of the Cincinnati Society for Medical Research and the Cincinnati branch of the American Chemical Society); the University of Illinois; Columbia University, the College of Physicians and Surgeons and the College of the City of New York in New York City; Johns Hopkins University and the Johns Hopkins Medical School in Baltimore; the University of Chicago; the Ohio State University; McGill University; the Mellon Institute of the University of Pittsburgh; the University of Nebraska; the University of Kansas; before the American Chemical Society in Indianapolis; before the National Academy and the American Chemical Society in Washington.

If I have omitted any institution or scientific body to which I had the pleasure of addressing myself and which in consequence did its share toward making possible the lectures given in this volume, I ask pardon. I admit that I had difficulty in remembering everything that happened to me while living at what seems to be the customary American rate. I need to express my appreciation, also, of invitations received from the Massachusetts Institute of Technology, the University of California, Syracuse University and a number of others — invitations which I regret it was impossible to accept.

It hardly needs to be emphasized that upon such a tour the lecturer learns quite as much as his audience. The necessity of having his material so easily in hand that he may vary it according to the type and special wishes of his audience, or according to the time at his disposal, or to suit the viewpoint from which it is expected that his subject shall be handled — these things are of the greatest value to the lecturer himself. There is obviously much difference between the half-popular dissertation on colloid chemistry which is given twelve or thirteen hundred freshmen foregathered in a building ordinarily used for religious exercises and the talk which is given so select an audience as the American National Academy and the American Chemical Society meeting in the spacious halls of the Cosmos Club. And the theme of colloid chemistry is itself made to wear a different face, depending upon whether one talks the week through in Pittsburgh to workers interested chiefly in technical problems or whether one tries in two hours in the Johns Hopkins Medical School in Baltimore to discuss the relationships of colloid chemistry to biology and medicine.

Besides such possibilities for arranging and rearranging his materials, other advantages accrue to the lecturer. He is in this way enabled to determine by experiment, as it were, what is the best form and the most easily intelligible one in which he can present his remarks, and what are the facts and thoughts which interest his audience most. He needs but to observe how it reacts to his mode of presentation. He soon discovers what of that which he presents is not clear to his audience, is superfluous, or unduly long; what, on the other hand, interests them most; and in the discussions which follow a lecture he soon discovers whether he has succeeded in making his main argument clear. These things are possible, of course, only when the psychological experiment can be made many times. How fruitful may be such an experiment tried in succession upon a series of new audiences is best evidenced, perhaps, by the fact that in the course of these lectures both the choice of material and its disposition in the various lectures underwent a steady change. It may fairly be said that what has been chosen for presentation in this volume is the product of this experience. This, and the generous request of American friends that I print them, has led me to select the five lectures which I gave most often, to dictate them and to bring them out in this form.

There already exist a number of strictly scientific textbooks treating of colloid chemistry and a number of more or less valuable introductions to colloid chemistry of a popular or semi-popular nature. So far as I know, however, *none of these has tried to establish the right of modern colloid chemistry to existence as a separate and independent science while emphasizing at the same time its great possibilities of scientific and technological application. The attempt to give a general survey of modern colloid chemistry as a pure and as an applied science and in a form readily intelligible to the general reader seems to be new.*

This volume makes its first appeal to such readers as have heard little or nothing of colloid chemistry. It was to several thousand of just such that I gave these lectures, and it was through frequent contact with them that I was led, time after time, to change my mode of presentation, and, I hope, to improve it. I had, however, another reason for thus addressing myself to such readers. There still exists, I think, too great an hiatus between the true significance, importance and application possibilities of modern colloid chemistry and the knowledge which the public has of this science. It is a fair statement that every scientifically cultured individual knows something about radiochemistry. But that with radio-chemistry there was born a twin science, the fruits of which are no less wonderful and the application possibilities of which to all possible branches of science, to technology and to industry are not only equal to but exceed those of radio-chemistry — this seems still largely unknown to the general public. I do not hesitate in consequence to designate this volume *a propaganda sheet for colloid chemistry.*

I am also presumptuous enough to believe that I shall, through this book, be able to render some of my colleagues in colloid chemistry a small service. It is a cause for rejoicing that the colloid chemist is being asked more and more frequently to address audiences upon the general fruits of modern colloid chemistry. These lectures may, perhaps, render him aid in such circumstances. I would especially emphasize the rather lengthy footnotes in which experiments are frequently discussed which have the great merit of always "going." I have also written into this volume a number of not previously published opinions and experiments which the expert worker in colloid chemistry will readily discover for himself; and in the footnotes I have often tried to give expression to suggestions which come into one's mind, one might almost say automatically, whenever one works long and hard in a given field. But the professional colloid chemist will, perhaps, be most interested in just what concepts and facts I chose for presentation, because they seemed to me to be especially characteristic of modern colloid chemistry.

Because of the wealth of colloid-chemical papers and books, I could not hope to give references to more than a few. In choosing those which I did, I have selected for the most part such papers and larger texts as contain summaries of investigations and are ready guides to further literature.

May this volume serve my readers as a guide into a long-existent but, until recently, scarcely recognized world of remarkable phenomena and wondrous mental concepts.

WOLFGANG OSTWALD.

GROSSBOTHEN, WALDHAUS
July, 1914.

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FIRST LECTURE.

FUNDAMENTAL PROPERTIES OF THE COLLOID STATE. COLLOIDS AS EXAMPLES OF DISPERSED SYSTEMS. METHODS OF PREPARING COLLOID SOLUTIONS.

I HAVE had the honor of being asked to tell you something of a new branch of physical chemistry, namely, colloid chemistry. Although I know full well that one should never begin a lecture with an apology, I feel that a few remarks are necessary before I enter upon my main theme.

As you know, colloid chemistry is a relatively young science. Colloid chemistry was officially founded by the Englishman, THOMAS GRAHAM, some fifty years ago. Various papers, it is true, were written even earlier on subjects which we today regard as colloid-chemical. I need but to call to your mind the contributions of the German, BENJ. JEREMIAS RICHTER, and of the Italian, F. SELMI, which appeared in the beginning of the nineteenth century. Yet it is only in the last fifteen years that the facts of colloid chemistry have become sufficiently large in number, that their relationships to each other have become sufficiently plain, and that laws regarding their behavior have been discovered which justify a discussion of colloid chemistry as a separate branch of science.

But, though still so young, the phenomena and the ideas incorporated under the term colloid chemistry are many. It is an almost universal complaint that colloid chemistry has already, — I beg you to note, *already*, — become so great that no one man can master it in its entirety. Especially does the beginner find it difficult to get about in the confusing mass of colloid-chemical facts and theories. Nor has this rapid development in any sense ceased or even abated. The reverse is the case. New facts and new ideas are born daily as they were ten years ago, and a couple of colloid-chemical journals and some dozen text-books appear as the mere beginnings of attempts to organize and classify the available riches. No one knows this better than the authors and founders of these text-books and journals.

This is the point which I should like to emphasize before attacking my actual problem. It is impossible in my short series of lectures to give more than an outline of colloid chemistry. One can lecture for two semesters on this subject without doing it justice. It is far easier to give many lectures on colloid chemistry than only a few. What I bring you must represent a mere instantaneous photograph of what I regard as modern colloid chemistry. This fact may disappoint those specialists among you who would like detailed discussion of some of its special problems. I have, however, been told that what most of my audience desires is a survey of the field, so that what I say represents an effort to meet this wish.

§1.

The first question raised by any one approaching the field of colloid chemistry is this: what are colloids? About the same feeling is expressed in the questions: what are the most important characteristics of a colloid? Or, how can one determine quickly and simply whether or not a given substance is a colloid? This first lecture will attempt a clear and concise answer to these fundamental questions. To some of you it may appear that a whole lecture is too much to devote to these questions. I could, of course, be more brief were I simply to make two or three statements defining the concept *colloid* according to our present-day beliefs and were I then deductively to analyze and explain them. But such a deductive method of reasoning would, to me at least, seem stupid. I believe that you will like it better if I try to present the development of our concept in a more inductive and experimental manner. The answer to the question is by no means as simple and elementary as might at first appear. It has changed markedly with time and is today quite different from what it was in GRAHAM'S day or in the older text-books. How important it is to obtain a clear and short definition of the term colloid is clearly betrayed by the fact that there is often no end to debates in colloid chemistry because different authors have each different notions of what really constitutes a colloid.

One might, at first sight, think it possible to decide whether a given substance is a colloid or not on the basis of its general chemical or physical properties. The word *colloid* is derived from the Greek κολλα meaning glue. Thus one might think that all chemically complex substances are colloids. This conclusion is partly justified; it is not, however, universally true. More important yet is the fact that while complexity of chemical constitution is likely to give rise to the colloid state, the converse does not follow. Among the many colloids I show you here,[1] you observe a whole series of very simple chemical composition (demonstration).

[1] I had at my disposal many dry colloids prepared by PAAL'S method with the aid of protective colloids. Simple solution of a few granules of these (when necessary with the application of heat) yields beautiful and lasting demonstration solutions. PAAL preparations of the various metals, metalloids, of mercury chromate and of manganese dioxid are easily purchasable. It is also easy to get colloid preparations of iron hydroxid (under the name of dialyzed iron oxid) and colloid carbon dispersed in an aqueous dispersion medium (india ink, aquadag) or in a mineral oil (ACHESON'S oildag). One can also buy colloid dyes like congo red, benzopurpurin, night-blue and alkali-blue. It is an easy matter, also, to prepare colloid sulphids of the various metals by working with very dilute solutions containing a trace of gelatin. The same is true of colloid berlin blue, of silver iodid ($KI + AgNO_3$) and of silicic acid ($Na_2SiO_3 + HCl$). Examples of the so-called hydrated emulsoids (like gelatin) are also easily obtainable. These may be dissolved in cold water or when necessary, in hot. In the group with gelatin belong agar, starch, gum arabic, serum albumin, casein (dissolved in dilute alkali) and rubber. Collodion, viscose, etc., are also easily obtainable. The preparation of red and blue colloid gold is discussed in the main text. Regarding further materials for demonstration see WOLFGANG OSTWALD, Kleines Praktikum der Kolloidchemie, Chapter IX, Dresden, 1920.

We have here colloid sulphids of the heavy metals, and here a whole series of colloid elements like gold, silver, sulphur and carbon. As of especial interest I show you colloid sodium chlorid, both as a milky liquid, and as a jelly of remarkably beautiful color.[1] No one, of course, will attribute to sodium chlorid a complex chemical constitution, and yet you see it here in colloid form. Colloid water or colloid ice can also be prepared through the rapid chilling of toluene which contains water, or by pouring water into liquid air.[2] There exists, therefore, no definite connection between chemical constitution and colloid state. In colloid chemistry things are, therefore, different from those obtaining, for instance, in radiochemistry, where, as you know, the observed phenomena are largely limited to elements of high atomic weight.

It is also impossible to make a list from which one might then discover whether or not a given substance is a colloid; attempts at this were made years ago, but proved unsatisfactory from the start. Why is such the case? It is because we already know too many colloids to make such cataloguing possible. While the preparation of a single new colloid was formerly regarded as of great interest, we are

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[1] This milky colloid sodium chlorid was prepared by C. Paal's method (see The Svedberg, Herstellung kolloider Lösungen, 346, Dresden, 1909). A simpler and quicker method is that of L. Karczag, Biochem. Zeitschr. **56,** 117 (1913) which yields a particularly beautiful jelly-like colloid. Judging by my own experience, it is best to use thionyl chlorid and sodium salicylate, which on double decomposition yield sodium chlorid and a complicated volatile thionyl ester. The dry sodium silicate is simply added to a few cubic centimeters of thionyl chlorid in a test tube, the sodium silicate being allowed to dissolve in the liquid through application of gentle heat. When about 0.5 gram of the salt is added to 5 cc. of the liquid, there results, after cooling for an hour or two, a beautiful glass-like solid jelly exhibiting in striking fashion the so-called Christiansen refraction colors (for example, green by reflected light, red by transmitted light, etc.). These gels will keep in a closed tube for some weeks. If benzol, ligroin or some other substance is used as a diluent, the colloid tends to go to pieces more quickly than if this is not done.

[2] See Wolfgang Ostwald, Handbook of Colloid Chemistry, trans. by Martin H. Fischer, second English edition, 106, Philadelphia, 1919, where references to the literature may be found.

today familiar with methods by which we can at will convert whole classes of substances into colloids. There is little doubt that we have often worked with colloids and still do so without being aware of it. This is true, for example, of many of the dyes and of other organic substances of complicated chemical structure. Depending upon the kind of solvent used, depending upon the concentration chosen in any given solvent, one and the same substance may appear either as a "colloid" or a "non-colloid." Tannic acid, for example, is colloid in water but not in alcohol; a simple crystallizing organic salt like tetraamyl-ammonium iodid is colloid in benzene, non-colloid in acetone even though it can be recrystallized from both solvents (P. WALDEN); while a sulphonic acid studied by the Swedish investigator H. SANDQVIST behaved in dilute aqueous solution as a normal electrolyte but in higher concentration not only as a colloid but as a crystalline liquid.[1] Chemical constitution, obviously, does not determine the colloid nature of a substance. As we proceed we shall encounter additional reasons indicating why such a listing of colloids is impossible.

We might make attempts on other grounds to get an answer to our fundamental questions, but they would all prove unsatisfactory. From mere consideration of the chemical or physical properties of a substance, we simply cannot decide whether or not it is a colloid. *To make such decision we need to study the properties exhibited by colloid substances under experimental conditions — we need to make a short, qualitative, colloid-chemical analysis.* But when we do this we shall also get an answer to the question: how do we recognize a colloid? And by inductive and experimental methods we shall also get answers to the other questions: what are the important properties of a colloid, and, what are colloids anyway?

§2.

It is of interest that in making such a colloid-chemical analysis we use experiments which, in a certain sense, follow

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[1] H. SANDQVIST, Koll.-Zeitschr., **19**, 113 (1916).

the historical development of the whole subject. The concept colloid was born of experiments on diffusion. With the fundamental phenomenon of diffusion all of you are familiar. If the lower half of a cylinder is filled with the solution of a colored salt and pure water is then carefully poured upon it so that admixture does not occur, the salt slowly wanders upwards into the pure water even when all vibration, etc., is shut out.

THOMAS GRAHAM was among the first to experiment extensively in this field and to follow his results quantitatively. An important element in GRAHAM'S work lay in the fact that he studied many different kinds of substances. He noted great quantitative differences in their diffusibility. While some dissolved substances, such as salts, acids and bases, showed a considerable diffusion velocity, he noted little or no diffusion in the case of gelatin, albumin, silicic acid and aluminium hydroxid. Those which diffused but little or not at all GRAHAM called colloids. This simple observation constitutes the foundation of the science of colloid chemistry.

It is easily seen that such diffusion experiments are hard to carry out quantitatively when the pure solvent is simply laid over a solution, for slight variations in technic and currents due to temperature differences disturb their accuracy. It is well-nigh impossible to demonstrate such experiments on "free" diffusion to a large audience. It is, however, possible to carry out these experiments in a more stabile form, the basic principle of which was also recognized by GRAHAM. It rests upon the fact that the velocity of diffusion in dilute gels — but only in *dilute* ones — is practically the same as in the pure solvent. I show you here several test tubes half filled with three per cent gelatin (demonstration). Upon them were poured a series of colored solutions which were then permitted to diffuse down into the gelatin for some days. You observe that the blue copper sulphate and the yellow picric acid have penetrated deeply into the gelatin. On the other hand, the tubes into which colloid gold, silver, iron hydroxid and congo red were poured show little diffusion. The series demonstrates clearly the different degrees of diffusibility of the different substances, just as Graham first observed. Let me emphasize at once that as shown in Fig. 1 these simple diffusion experiments prove of great service in any attempt to determine the colloid (*a*) or non-colloid (*b*) character of a given solution.

Fig. 1.—Diffusion of a colloid (*a*) and a "true" solution (*b*) into solid gelatin.

There is another way of overcoming the difficulties incident to experiments on free diffusion which permits, perhaps, a still sharper distinction between diffusing and non-diffusing substances. Presumably in an effort to overcome the experimental difficulties incident to his systematic study of many solutions Graham resorted to the following: Suppose we imagine a membrane of some sort, capable of taking up the solvent, to be introduced between a salt solution and its pure solvent. If a parchment paper tube, such as I show you here, is filled with a solution and the whole is then placed in a beaker filled with the pure solvent as shown in Fig. 2, it is clear that diffusion may occur through the parchment paper without being subject to disturbances due to vibration, etc., at the surface of contact between solution and solvent. Diffusion experiments of this type were also first made by Graham; in fact, he gave them a special name, calling the diffusion of dissolved substances through membranes, *dialysis*. He found that the substances capable of free diffusion passed through these membranes, while those incapable of diffusion did not. A distinction of noncolloid from colloid solutions could, therefore, be made by dialytic means. Such a parchment membrane is, obviously, nothing but a thin colloid membrane.

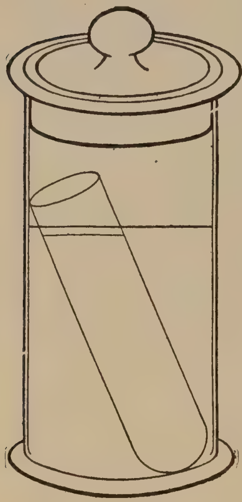
FIG. 2.—Dialyzer arranged for colloid analysis.

Parchment paper is, of course, not the only substance from which such membranes may be prepared. Pig bladder, fish bladder, sausage casings, reed tubes, or collodion may be used. They may be used in connection with and to cover special pieces of apparatus, such as bells or rings. I show you here a number of such dialyzers, directing your especial attention to two, constructed according to GRAHAM. To prepare artificially a dialytic membrane, as one of collodion, filter-paper capsules need simply be soaked in a collodion solution after which the solvent for the collodion is allowed to evaporate.[1]

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[1] Following the method of G. MALFITANO, collodion capsules are best prepared by dipping clean test tubes into liquid collodion. To get the collodion evenly distributed, the tubes are turned in the air while evaporation of the solvent is taking place. After being thus dried, the collodion films are stripped from the tubes. Dialysis thimbles may also be prepared by coating the inside of Erlenmeyer flasks with collodion and pouring off any excess. Everyone who has worked with these collodion sacks knows that their preparation is associated with a whole series of small technical tricks. The parchment thimbles of Schleicher and Schüll are convenient for many colloid-chemical purposes but are rather costly. They often have an acid reaction and should therefore be washed in boiling water before use. The saturation of filter-paper thimbles with collodion, as described in the text, is much simpler and cheaper, since filter-paper thimbles can be obtained in all sizes and are relatively cheap. What is most important, however, is that diffusion capsules thus prepared are very strong. They may also be used as osmometers.

Further improvements making for more rapid dialysis, employ the principle which I have described for the production of the so-called "spontaneous

As you see, we have already uncovered experimentally two characteristics of colloids. I imagine now that I hear you say: that is all very simple; colloid solutions are solutions which do not diffuse and which do not dialyze. This would constitute an experimental definition of colloid solutions. No doubt we have discussed two of the most important experimental characteristics of colloid solutions, but when we look at the problem more closely we discover that *these do not suffice* to characterize them fully. Moreover, a little thought reveals that this definition rests upon certain theoretical assumptions which may not be taken for granted. Let us take up this point for a moment.

§3.

Trouble arises from use of the word *solution* in our definition. What do we mean by this term? Let us for the moment free our minds of all special hypotheses regarding its nature. What we regard as characteristic of a solution is that it represents a *molecular distribution* of one substance in a second. Is this requisite fulfilled in the case of colloid solutions? Are "molecules" floating about in them? The older authors, including GRAHAM, believed this to be true even though they did, of course, think that there was some sort of a difference between the molecules of a colloid and those of a non-colloid. A first attempt to define this consisted in pointing out a possible physical difference between the molecules of the two, as illustrated, for instance, in the phenomena of allotropism. Sulphur, for example, in its different allotropic forms possesses different physical characteristics. There is, for example, rhombic and hexagonal sulphur and sulphur as $S\eta$ and $S\lambda$. In some such ill-defined manner GRAHAM and his followers accounted for the differences between the molecules of a colloid and a non-colloid solution. CAREY LEA, one of the best known of American colloid chemists, gave his paper on the colloid solutions of

ultrafilters" (Koll.-Zeitschr., **22**, 72, 143 (1918); see also the footnote on page 48).

metals the title, "Allotropic Modifications of Silver" actually meaning new colloid forms of it.

Suppose, for the moment, that we assume this view to be correct and that we actually do deal both in solutions of colloids and of non-colloids with molecules of the orthodox type but possessed of different physical properties. There really do exist many similarities between colloid and ordinary molecular solutions. Thus many colloid solutions like those of red gold, of congo red or of berlin blue are just as clear to the naked eye as molecular solutions of fuchsin or copper sulphate (demonstration). But colloid solutions also behave like ordinary molecular solutions in that *they pass unchanged through paper filters and even through most of the very fine porcelain or clay filters.* I can prove this to you with any of the colloids here on the table, as with this colloid gold or colloid indigo (demonstration). These phenomena emphasize the great similarities and close relationships between colloid and ordinary molecular solutions.

Let me show you an experiment which will recall your first days in qualitative analytical chemistry. I have here a saturated solution of mercuric cyanid to which I add some hydrogen sulphid. You see that mercuric sulphid is produced (demonstration). A thick precipitate is formed which quickly settles and which we can then readily filter off (demonstration). Only a practically colorless solution passes through the filter. Let me now repeat the experiment, but this time I shall use a very dilute cyanid solution (demonstration). As you see, mercuric sulphid is again produced which must this time also be solid for it is insoluble in water or in a dilute solution of hydrocyanic acid. I again pour the dark brown solution upon a filter, but you observe, we encounter what is so unpleasant to the analyst: the precipitate goes through (demonstration). What are we to do? Is the "notoriously" insoluble sulphid of mercury prepared from the dilute solution *also* a colloid? We know that it is a precipitate, and a precipitate of a solid substance, for mercuric sulphid at room temperature and in the presence of water can be nothing else. If the concentration is merely raised, or the solution is left to itself for a time, or if we add salt, we obtain a solid precipitate from this brown liquid, as every analyst knows, yet this brown liquid which has passed through the filter and which contains the sulphid precipitate looks just as clear to the naked eye as any ordinary filtered molecular solution. We can also carry out diffusion and dialysis experiments with this finely-divided precipitate, for it will keep for days.

In the series of tubes illustrating diffusion there is one filled with just such a mercuric sulphid precipitate as we are discussing and you notice that none of it has wandered down into the gelatin. The precipitate therefore behaves like a colloid in this regard also. But may we under the circumstances still continue to speak of molecular division? Are all the other colloids we have before us nothing more than such finely-divided precipitates — the idea seems rather plausible — *are they nothing but very fine suspensions of insoluble substances, nothing but "mechanical" suspensions or emulsions produced by mixing an insoluble solid or liquid into a second liquid menstruum?* No doubt these facts will convince you that inability to diffuse and to dialyze are alone *not sufficient* to characterize colloid solutions. Mere suspensions of finely-divided precipitates also do not diffuse or dialyze.

§4.

Connected with these peculiar relations of the colloids to the ordinary solutions and of the colloids to the mechanical suspensions there is a most interesting and vital debate. On the one hand, investigators have tried to make colloid solutions simply a subdivision of molecular solutions and something different from "mechanical" suspensions; on the other hand, another group has emphasized the similarities between mechanical suspensions and colloids and placed these two together over and against the molecular solutions. Their views may be indicated as follows:

They have all tried, in other words, to group the three types of substances under two headings. The discussion has at various times leaned now to one side, now to the other, as the one or other partisan believed he had at last discovered a conclusive difference between the two classes. Thus, suspensions of the coarser precipitates are rather turbid, while many colloids are clear to the naked eye. But even FARADAY learned to use a special method of illumination which permits the recognition of slight turbidities, and so was able to show that red colloid gold is also turbid. Those who grouped colloid solutions with the suspensions at once used this fact as evidence for the correctness of their view. On the other hand, those who grouped the colloids with the true solutions pointed out that in typical, filterable colloids one can no longer make out the individual particles under the microscope, and they used this in support of *their* view. It was a believer in this view, R. ZSIGMONDY, who was able by optical methods to demonstrate the presence of individual particles in typical colloids, and so again to prove the inadequacy of this classification.

The discussion has not yet been settled. But most interesting is the fact that not a single colloid chemist any longer troubles about it. The discussion has simply disappeared. And why? *Because modern colloid chemistry teaches that there are no sharp differences between mechanical suspensions, colloid solutions and molecular solutions. There is gradual and continuous transition from the first through the second to the third. It is best to regard all three from the same viewpoint and first to emphasize their similarities. After this has been done, their special peculiarities may be taken up.*

This constitutes, perhaps, the most important conclusion of our whole modern colloid chemistry. In this lecture I can only ask you to take my word for the truth of this continuity of the three classes. The next will be largely devoted to proving it to you.

§5.

What now is there common to suspensions, colloid solutions and molecular solutions?

Briefly stated, *the physical and chemical properties change in periodic fashion in all three.* Let us imagine a suspension of quartz particles in water. Were we to measure, by appropriate means, the changes in the coefficients of refraction in such a suspension and plot the results, we should obtain such figures as are shown in Figs. 3 and 4. We

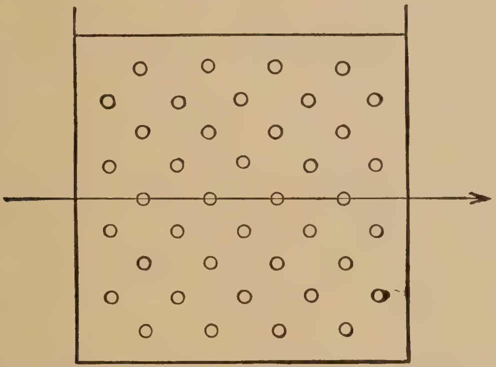

Fig. 3. — Diagram illustrating the concept, dispersed system.

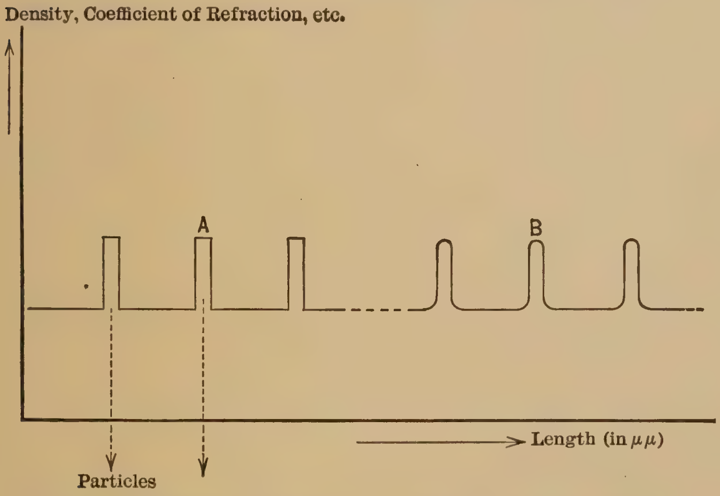

Fig. 4. — Diagram illustrating the concept, dispersed system.

should encounter a periodic increase and decrease in the coefficient of refraction depending upon whether we were striking a quartz particle or the suspending medium. The same periodic change, not only in the coefficients of refraction but in all other physical and chemical properties, would be encountered, no matter in which direction we went through the quartz suspension. But such periodic changes in properties would also be encountered in any solution in which the substances are in a state of molecular division. In molecular solutions, too, must appear points where the physico-chemical properties of the solvent predominate, and again others in which the properties of the dissolved molecules, combined perhaps with the solvent, predominate. Thus in such an electrolyte as a dilute salt solution we know that the positive and negative electricities must follow each other in succession. Other physico-chemical properties, like density, must change similarly, but such periodic changes in a molecular solution must occur within smaller spaces (within what we call molecular distances) than in a quartz suspension. What has been said regarding suspensions and molecular solutions must hold for colloid solutions also. In all three the physical and chemical properties show periodic changes in space.

§6.

This view is a central one in modern colloid chemistry. Colloid chemistry speaks of the *disperse structure* of these solutions, applying to them the general terms *dispersed systems* or *dispersoids.* A dispersed system is therefore nothing more than one in which the properties change periodically in space.

To address myself for a moment to the physical chemists among you, it is clear that this definition is more inclusive than that represented by the terms "polyphasic" or "heterogeneous." When we speak of a polyphasic system, as represented, for instance, by a quartz suspension, we mean that periodically a *whole series* of properties changes at once. Practically *all* the physical and chemical properties change as we pass from the one phase into the other. But our concept of dispersion makes no assumptions whatsoever regarding either the kind or the number of the properties which are changed in space. If you will call to mind, for example, that RÖNTGEN rays are regarded as little more than oscillating systems of electrically-charged masses, the electrons, you will observe that it is possible to construct dispersed systems which consist, practically, of but one form of energy.[1]

The term dispersed system is valid, therefore, not only for so-called "heterogeneous" systems but also for "homogeneous" ones, as represented by molecular solutions. The term means less than heterogeneity, yet it contains more than the term homogeneity. This discussion may sound too theoretical to please you, but I believe that you will soon recognize for yourselves how illuminating it is when applied to the problems which we are about to take up, and how fruitful are its practical applications.

§7.

Coarse suspensions, colloid solutions and molecular solutions are all to be regarded as dispersed systems and to be studied together under this common heading. In this fashion all the old quarrels arising out of the attempt at classification of the colloids on a dualistic basis are disposed of.[2] But how do the three types of systems differ from each

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[1] The concepts of quantity which have recently been applied to different kinds of energy and combinations of energy are adaptable, in large measure, to dispersed systems, provided it be remembered that, as ordinarily used, the term "quantity" embraces only units possessing a maximal degree of dispersion.

[2] It has been argued occasionally that this expansion of colloid chemistry to dispersoid chemistry is a matter of words only and that I have merely introduced the "useful terms" dispersed system, dispersion medium, degree of dispersion, etc. But the reader will perhaps see for himself (from the first and second chapters of this volume, for example) that the mere business of words is as nothing compared with the importance of the *concepts* which have been developed.

other? They differ, first of all, in the *number* of the periodic changes encountered in the unit volume. As is readily apparent, the number of periods, or *the degree of dispersion*, increases while we pass from the coarse suspensions through the colloids to the molecular solutions, as shown in the following diagram.[1]

DISPERSED SYSTEMS.

Coarse Suspensions · Colloids · Molecular Solutions

⟶

Direction of increasing degree of dispersion

The degree of "subdivision" of physical and chemical properties is greatest in the molecular systems and least in the coarse suspensions. Molecular systems belong to the *most highly* dispersed, coarse suspensions to the *least* dispersed systems. Colloid solutions occupy a middle position. There is, of course, not the slightest reason for assuming that any sudden change occurs in degree of dispersion as we pass from the coarsely dispersed to the colloid systems, or from these to the molecular. Not only is there no theoretical reason against such a view, but there is no practical one either. As I shall show you in detail in the next lecture, *we know dispersed systems of every degree of dispersion in nature.*

It is well, perhaps, to give you some concrete illustrations of this. I show you here a series of different kinds of sulphur (demonstration). In this first bottle I have the familiar large yellowish-green crystals; their structure is so coarse that we can hardly speak of them as dispersed systems. In this second bottle I show you sticks of sulphur; these have a crystalline structure but the crystals are already so highly dispersed that they are hardly visible to the naked eye. This third bottle contains flowers of sulphur which represent under-cooled droplets of sulphur that are but fractions of a

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[1] The lecturer will obviously not write this diagram anew in every lecture but simply develop it from a single diagram mounted once and for all time before the audience.

millimeter in diameter; they show, in other words, a *microscopic* degree of dispersion. Here I show you *colloid* sulphur in a watery "dispersion medium"; it is a milky liquid from which the sulphur separates out only very slowly; in a drop of it placed under the microscope you do *not* see any particles; this system is therefore still more highly dispersed than the preceding one. The fifth bottle contains another largely colloid sulphur, namely, sulphur dissolved in benzol; it is a scarcely turbid, yellowish fluid in which the sulphur is still more highly dispersed than in the watery solution.[1] And here, in this sixth bottle, I show you *molecularly* dispersed sulphur, in the form of the well-known solution of sulphur in carbon disulphid.

You observe, therefore, how one and the same substance may appear in all possible degrees of dispersion. Other substances can, of course, also be made to assume different degrees of dispersion. For example, there are the large crystals of sodium chlorid, the more highly dispersed ones constituting common table salt, the colloid preparations of sodium chlorid that I have already shown you, and its ordinary molecular solution.

But these facts also show you how through our concept of the dispersed system our main problem of the relation of colloid solutions to molecular solutions and to coarse suspensions finds a simple answer. We pass from the one into the other gradually and it is entirely arbitrary at which point we decide to insist on lines of division between the three classes. On theoretical grounds we cannot say what degree of dispersion is characteristic of any one of the classes. On practical grounds, however, we can settle upon values which are suitable as a basis for division. These coincide with degrees of dispersion at which certain *methods* used in the investigation of dispersed systems either fail or can first be used to advantage.

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[1] See J. Amann, Kolloid-Zeitschr., **8,** 197 (1911).

§8.

A practical division between coarsely dispersed and colloid systems can be made, for instance, microscopically. It follows from the theory of microscopic vision that we cannot see individual particles of a diameter of less than half a wave length of light. By employing micro-photographic methods which enable us to work with the short waves of ultra-violet light, we obtain as the limit of microscopic vision a value of about one ten-thousandth of a millimeter or 0.1 μ. This value is used — let it be noted, altogether arbitrarily — as marking the transition from coarse to colloid dispersions. Other methods of investigation, such as filtration, yield similar values. The pores of the best grades of hard filter paper (No. 602 of Schleicher and Schüll) are about 1 μ in diameter; those of clay and porcelain filters about 0.2 to 0.4 μ. These values therefore approximate those obtained by microscopic means. It is characteristic of typical colloids that they pass through these filters while coarse suspensions do not.

If now we seek a line for the division of colloids from molecularly dispersed solutions, we may begin by asking the physical chemists about the size of molecules. By methods which we cannot discuss here, they have decided that typical molecules have a diameter of one ten-millionth to one one-millionth of a millimeter, in other words 0.1 to 1.0 $\mu\mu$. The diameter of a very large molecule like that of starch has been calculated as 5 $\mu\mu$. But, as you know, starch dissolved in water shows marked colloid properties, so this value comes within the realm of colloid dimensions. We are familiar with colloid-chemical methods to be discussed later, like optical ones, for example, which also begin to fail us when we reach dimensions approximating one one-millionth of a millimeter. It has, therefore, been agreed, again arbitrarily, of course, to draw the line between colloid and molecular at this point.

The region of dispersity within which the colloids lie is therefore bounded by particles having, on the one hand, a diameter of one ten-thousandth of a millimeter, on the other one of one one-millionth of a millimeter, as indicated in the following diagram:

DISPERSED SYSTEMS

Coarse Dispersions Colloids Molecular Dispersoids.

$\longrightarrow$

Increase in degree of dispersion

↓ 0.1 μ to 1.0 μμ ↓

Coarse Dispersions	Colloids	Molecular Dispersoids.
Periods greater than 0.1 μ; do not pass through paper filters; microscopically analyzable.	Pass through paper filters; cannot be analyzed microscopically; do *not* diffuse or dialyze.	Periods smaller than 1.0 μμ; pass through filter paper, cannot be analyzed microscopically; diffuse and dialyze.

Dispersed systems lying within these middle limits are called *typical* colloids, but let me again emphasize that we deal with purely arbitrary divisions and that we are familiar with transition systems of every degree of dispersity not only between coarse dispersions and colloids but between these and molecularly dispersed systems.

§9.

We are now able to answer the question raised at the beginning of this lecture: what are colloids? *According to modern colloid chemistry they belong, with mechanical suspensions and molecular solutions, to the group of the dispersed systems, differing from the suspensions and the molecular solutions only in the special value of their degree of dispersion.* This is the theoretical definition of the colloids. From an experimental point of view — and under this heading we shall get the answer to our questions regarding the means by which we may recognize colloids — *the colloids differ from the coarse dispersions in that they cannot be analyzed microscopically and in that they pass through ordinary filters. The colloids differ from molecularly dispersed systems in that they do not diffuse and do not dialyze, which molecular solutions do.* But should you ever find occasion to express or to make use of this modern definition, do not forget to add that *there exist transition systems not only between coarse dispersions and colloids but between colloids and molecularly dispersed solutions. The colloids merely represent a realm differentiated for practical purposes from a continuous series of systems.*

If all this is true, some important corollaries follow. If colloids are "nothing but" systems of a certain sub-molecular degree of dispersion, it follows that *every substance may appear in the colloid form or be made to appear so*, for, theoretically at least, we know that for every substance there must exist a second substance in which the first is not spontaneously soluble in molecular form. You can see for yourselves how well experience bears out this conclusion. The table here is covered with a fairly large number of colloid preparations and I have told you that there are many hundred others. There are so many that it is impossible to list them all. These facts are the best sort of confirmation of the teaching that every substance may be obtained in colloid form, or expressed in the words of the Russian investigator, P. P. von Weimarn: *The colloid state is a universally possible state of matter.*

§10.

Our diagram of the dispersed systems also enables us to predict by what general *methods* a given substance may be brought into the colloid state. There are two such. We may begin with a non-dispersed or coarsely dispersed system and increase its degree of dispersion until colloid dimensions are reached, or we may start with a molecular system and allow the molecules to combine, aggregate or condense until the colloid state is reached. Their further growth is then interrupted. The former of these is known as the dispersive, the latter as the condensive method of producing colloids.[1]

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[1] This general distinction between condensive and dispersive methods of preparing colloid solutions originated with The Svedberg.

Many different methods, or, better expressed, many different types of energy may be used either to disperse or to condense the molecules of any substance. Colloids may be prepared by employing not only mechanical energy but chemical or electrical energy, or even heat and light. Of the many possible methods I can show you but a few. I shall show you a *chemical condensation* method and an *electrical dispersion* method.

A particularly interesting colloid is that of gold which I have already showed you as an intensely reddish-violet or bluish liquid. This colloid gold was prepared even in the days of the alchemists by the reduction of gold salts with all kinds of organic substances, such as urine. B. J. RICHTER, M. FARADAY and many other investigators have since then studied it. In order to obtain it by a method of chemical condensation I begin with a molecularly or ionically dispersed solution of gold chlorid to which sodium bicarbonate has been added until neutral to litmus. I need now to reduce the gold chlorid to metallic gold, but this must be done in such a way that the resulting gold remains so highly dispersed as not to exceed colloid dimensions. As you know, gold chlorid may be reduced by many different kinds of substances, especially organic ones. You need but dip your finger into the solution when it becomes stained a bluish-violet by the colloid gold produced through the reducing action of the organic substances contained in the skin. You are frequently told in colloid chemistry that the preparation of fairly stabile colloid gold is a delicate undertaking, for which not only the purest distilled water is necessary but accurate quantitative work as well. If these things are ignored, red gold is rarely obtained, but violet or blue gold appears instead. I want to show you a method by which we can always obtain red colloid gold even when we work but roughly.

This Erlenmeyer flask contains about 100 cc. of ordinary distilled water. I add a few drops of a neutralized one per cent solution of gold chlorid, and, after mixing, a few drops of a very dilute solution (about 0.1 percent) of tannin. We need not work any more accurately than this. Only not too much gold chlorid or too much tannin must be used. The completed mixture should be practically colorless (demonstration). I now heat it over a Bunsen burner for one or two minutes, shaking it constantly. You observe that even before the mixture begins to boil it assumes a cherry red color. I may now add more gold chlorid or more tannin as necessary and thus obtain an almost reddish-black solution. The experiment will succeed even with ordinary tap water.[1]

You may be interested in knowing how blue or violet gold is prepared. A method which furnishes blue gold, as certainly as the previously described experiment yields red, consists in adding a few drops of a very dilute solution of hydrazin hydrochlorid to a dilute, neutral solution of gold chlorid. The blue color appears almost immediately if enough of the reducing material is added (demonstration). If I add but little, a violet color is obtained. If too concentrated solutions are employed, the gold becomes bluish-black or greenish-black. It is then no longer colloid but precipitates out in microscopically visible particles.[2]

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[1] This method for the production of stabile red colloid gold is interesting because it really "works" every time, provided only neutralized gold chlorid is used and the work is carried out in sufficiently great dilutions. If the red color does not appear immediately after heating, more tannin and more gold chlorid may be added alternately without endangering the possibilities of getting the desired red color. It must be cautioned that the hot solution may not at once be diluted with cold water. This is likely to bring about a change from the cherry red to violet. After the colloid solution has been cooled, dilution will not markedly affect the color. This assured method for producing red colloid gold (I have performed the experiment countless times with all kinds of materials and even when only tap water was at hand) seems not, as yet, to have been described in the literature. Its success seems to depend upon the fact that the tannin acts not only as a reducing substance but, to a certain degree, also as a protective colloid.

[2] This method also always "works." A tiny crystal dissolved in some 20 cc. of water yields a solution which for most purposes acts as a sufficiently strong reducing mixture. For other simple methods see Wolfgang Ostwald, Kleines Praktikum der Kolloidchemie, 2, Dresden, 1920.

These demonstrations illustrate chemical condensation methods. We begin with molecularly dispersed systems, free the gold molecules and then allow them to coalesce into larger aggregates. We choose the conditions for our experiments so that the aggregation does not proceed to the point of yielding coarsely dispersed precipitates but *ceases* as soon as the condensation has attained colloid dimensions. What are the experimental conditions which must be maintained in order to attain this end?

You have seen for yourselves that I have worked only with dilute solutions. As I emphasized in the experiment on the precipitation of colloid mercuric sulphid, we obtain a colloid precipitate which will pass through the filter only if the precipitation is produced in very dilute solutions. Let me show you another example of this dependence of degree of dispersion of the precipitate obtained upon the concentration of the reacting solutions.

I have poured together in this first beaker two very dilute solutions of iron chlorid and potassium ferrocyanid. The resulting precipitate of berlin blue is so highly dispersed — it is a colloid — that the liquid is intensely blue yet appears perfectly clear to the naked eye (demonstration).[1] In this second beaker I have poured together two somewhat more concentrated solutions of the same materials. You observe that a bulky, dark-blue precipitate has formed, above which there remains the slightly colored dispersion medium. Evidently, therefore, *the degree of dispersion* is less in this second beaker, while the *size* of the individual particles of the precipitate has been increased, simply by working with more concentrated solutions of the reacting materials.

I show you now two still more highly concentrated, practically saturated solutions of the two reagents. When

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[1] For demonstration purposes it is best to use large glass cylinders or parallel-walled museum jars. These should be lighted from behind by means of an arc lamp, the light from which is made to pass through ground glass or paper.

I pour these together[1] and stir with a glass rod (demonstration) you note a remarkable fact: the two liquids set to form a cheesy paste so stiff that I can turn the beaker upside down without losing its contents (demonstration). Please recall that the paste resulted from the mixture of two mobile liquids possessing in themselves no high degree of viscosity. I now make the following experiment: when I take some of this thick precipitate and stir it into a large volume of distilled water (demonstration) I again obtain a clear blue liquid which is fairly stabile and which is also colloid, as I can prove to you by filtering it (demonstration). It looks, therefore, as if, by the use of very highly concentrated reaction mixtures, the size of the precipitated particles is again *decreased*. This is really the case, as has been shown in detail by P. P. VON WEIMARN. The precipitate is coarsest when *medium* concentrations are employed. The size of its particles decreases both with decrease or increase in concentration of the reacting substances. A curve illustrating the relation of size of particles to concentration of the reacting solutions would, therefore, show a maximum in a region of medium concentration, as indicated in Fig. 5.

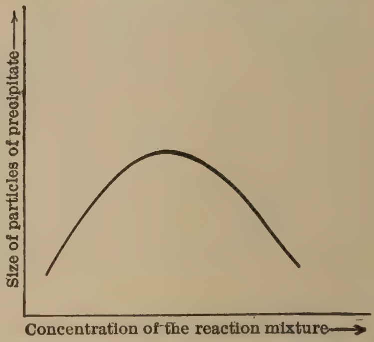

FIG. 5. — Influence of the concentration of the reaction mixtures upon the size of particles of a precipitate.

§11.

Because of the importance of this VON WEIMARN law in colloid synthesis by chemical condensation methods, I show you a number of microphotographs illustrating these facts

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[1] Since the saturated potassium ferrocyanid solution contains much less salt than the iron chlorid solution, about 2 cc. of the chlorid solution must be added drop by drop to 10 cc. of the cyanid. The iron chlorid is poured into the cyanid — not the other way about.

(demonstration).[1] The pictures are photographs of barium sulphate precipitates, made by pouring together barium cyanid and manganese sulphate. They show the changes in the character of the precipitate in passing from mixtures of dilute solutions to those which are more concentrated. Fig. 6 presents the precipitate formed on mixing $\frac{1}{2000}$ normal solutions. As you see, the picture shows *nothing.* This is just what it is intended to show. At this concentration we obtain a *colloid* precipitate of barium sulphate, and, since colloid particles are not visible microscopically, the photograph could, of course, show nothing. Fig. 7, obtained with $\frac{1}{1000}$ normal solutions, begins to show particles. The enlargement is about 1 : 1500. As we approach the higher concentrations of $\frac{1}{500}$ normal to $\frac{1}{50}$ normal (Figs. 8 and 9) we observe a gradual increase in the size of the particles. The photographs are all on the same scale and may, therefore, be compared directly with each other. At still higher concentrations, $\frac{1}{20}$ to $\frac{1}{10}$ normal, actual crystals begin to appear, as evident in Figs. 10 and 11. In these concentrations the maximum size for the individual particles has been attained. From this point on, as we pass through the higher concentrations of $\frac{1}{5}$, $\frac{1}{2}$ and $\frac{1}{1}$ normal, you observe that the size of the particles again decreases steadily (Figs. 12, 13 and 14). In still higher concentrations, such as $\frac{2}{1}$ to $\frac{7}{1}$ normal (Figs. 15, 16 and 17) we obtain the paste-like precipitates which I showed you in the case of berlin blue. The pictures of such precipitates appear as solid films torn in various ways. It is still possible to make out that these films consist of minute crystals. In the most highly concentrated, almost saturated solutions the microphotograph again shows nothing (Fig. 17).

It is amusing that in the classic German formulas for

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[1] See P. P. VON WEIMARN, Kolloid-Zeitschr., **2** (1907, 1908); see also his Zur Lehre von den Zuständen der Materie, Dresden and Leipzig, 1914. Not all the photographs appearing in the original are reproduced herewith. For lecture purposes it is best to project diapositives.

Fig. 6.

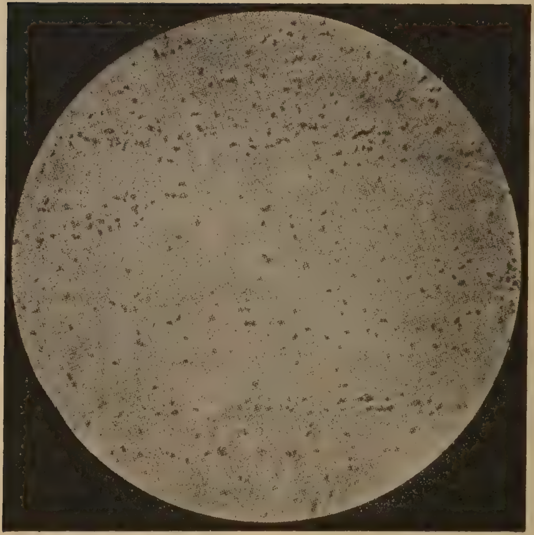

Fig. 7.

Fig. 8.

Fig. 9.

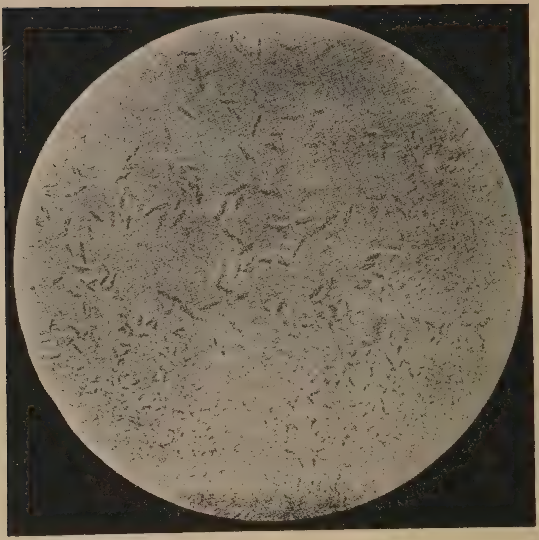

FIG. 10.

FIG. 11.

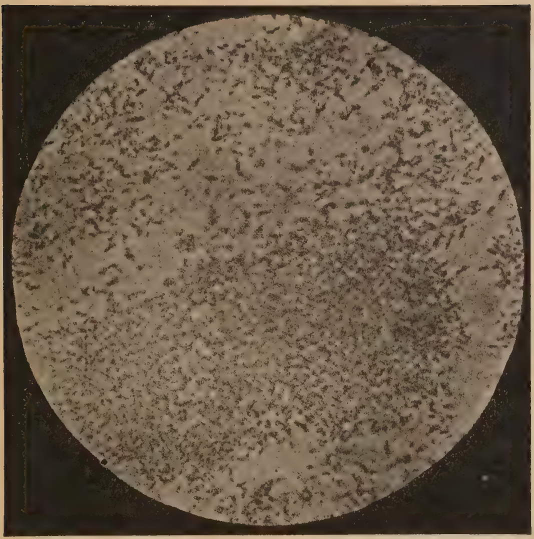

FIG. 12.

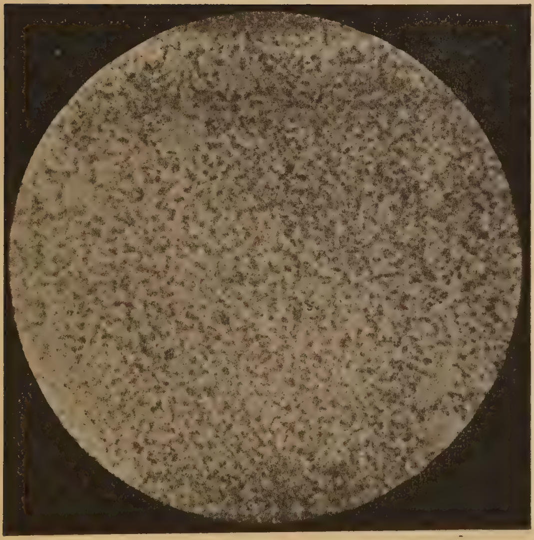

FIG. 13.

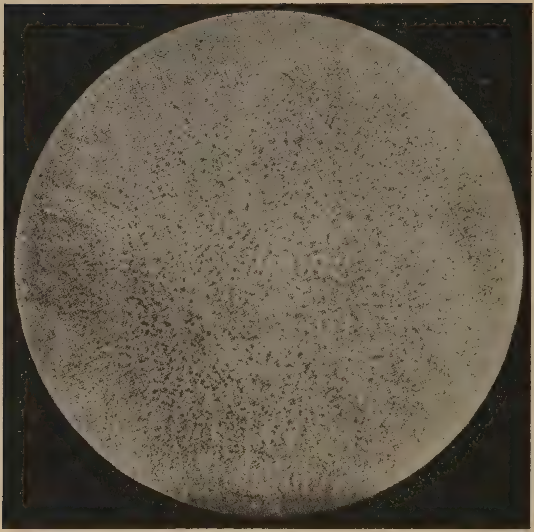

FIG. 14.

FIG. 15.

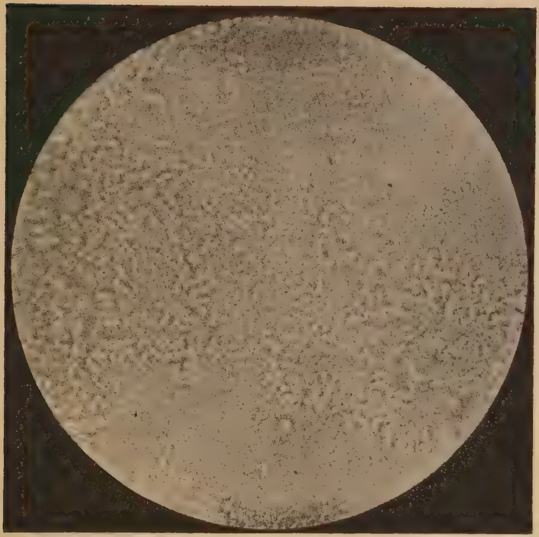

FIG. 16.

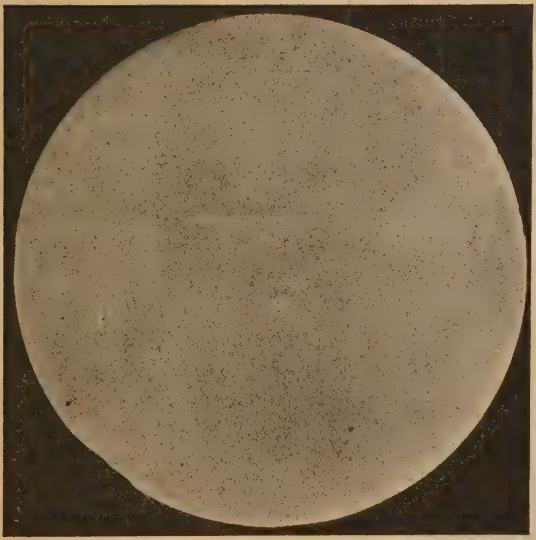

FIG. 17.

making colloid solutions through chemical condensation, very dilute solutions are always insisted upon while the formulas of the American colloid chemist Carey Lea are equally insistent upon the use of concentrated ones. In keeping with the American way of doing things Carey Lea's formulas begin by calling for several grams of gold chlorid.

§12.

I show you next a dispersion method of producing colloid solutions in which use is made of electrical energy. It is G. Bredig's method of dispersing metals. I have here two silver wires fastened into a stand in such a way that the ends may be approximated by turning a micrometer screw (Fig. 18).[1] A five- to eight-ampere current obtained by sending the ordinary 110-volt current through a rheostat is now sent through these wires. Their tips dip into distilled water which has been slightly alkalinized with a trace of sodium bicarbonate. I turn on the current, and by

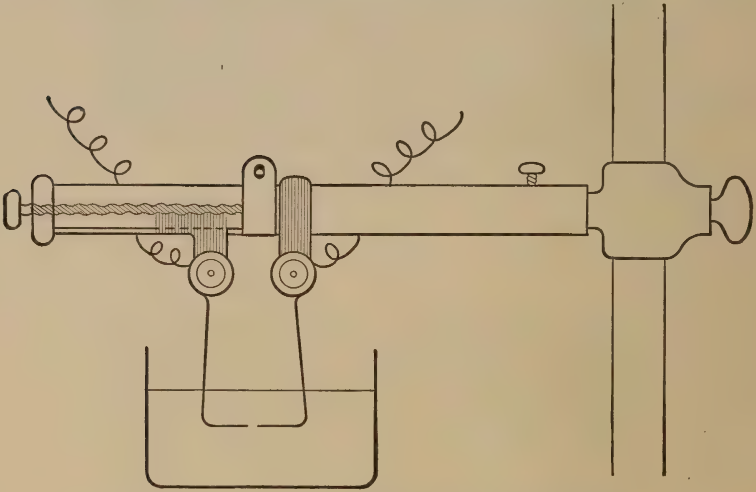

Fig. 18.—Apparatus for dispersing metals electrically.

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[1] This exceedingly useful arrangement was placed at my disposal by Professor J. Stieglitz in the University of Chicago.

regulating the micrometer screw, allow a tiny arc to form between the wire tips under the water (demonstration). You observe how dense dark brown or greenish clouds emanate from the tips of the wires and remain suspended in the water.

This greenish-brown liquid is one of colloid silver somewhat contaminated with colloid silver hydroxid. The solution is perfectly clear to the naked eye and passes easily through filter paper. Other metals may be colloidally dispersed in the same way; in fact by making use of special methods such as oscillating electrical discharges, low temperatures and organic dispersion media, The Svedberg has prepared even the alkali metals in the form of beautifully colored colloid solutions.

We can also prepare colloid solutions by exposing metal plates to ultraviolet light, by heating alloys and cooling them suddenly in water and by grinding powders for long periods of time.[1]

§13.

The main conclusions then to which this lecture has led may be summarized as follows:

Colloids are dispersed systems, in which the diameter of the dispersed particles in typical cases lies between one ten-thousandth and one one-millionth of a millimeter. They are distinguished experimentally from molecularly dispersed systems by the fact that they do not dialyze; and from coarse dispersions by the fact that they cannot be analyzed microscopically. Colloids pass through filters readily, while coarse dispersions do not. Transition systems exist between colloids and molecular

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[1] For a discussion of colloid synthesis through exposure to radiant energy see Wolfgang Ostwald, Grundriss d. Kolloidchemie, 1. Aufl., 302, Dresden, 1909; The Svedberg, Kolloid-Zeitschr., **6**, 129, 238 (1910); for the preparation of vanadic acid by sudden cooling see E. Müller, Kolloid-Zeitschr., **8**, 302 (1911); for the preparation of colloids by trituration see Wolfgang Ostwald, Grundriss der Kolloidchemie, 1. Aufl., 292, Dresden, 1909; see also C. Benedicks, Kolloidchem. Beih., **4**, 260 (1913), who describes the production of colloid gold by trituration as practiced in the seventeenth century, as well as G. Wegelin, Koll. Zeitschr., **14**, 65 (1914).

solutions and between colloids and coarse dispersions. The colloid state represents a universally possible state of matter. There is no reason why every substance may not be produced in colloid form. It may be accomplished either through the dispersion of non-dispersed or coarsely dispersed substances, or through the condensation of molecularly dispersed systems. To these ends not only chemical but mechanical, electrical and other kinds of energy may be used.

II.

CLASSIFICATION OF THE COLLOIDS.

THE PHYSICO-CHEMICAL PROPERTIES OF THE COLLOIDS AND THEIR DEPENDENCE UPON THE DEGREE OF DISPERSION.

SECOND LECTURE.

CLASSIFICATION OF THE COLLOIDS. THE PHYSICO-CHEMICAL PROPERTIES OF THE COLLOIDS AND THEIR DEPENDENCE UPON THE DEGREE OF DISPERSION.

The previous lecture dealt with the fundamental facts and problems of colloid chemistry. I tried to show you how the concept of the colloid has assumed a new meaning by having been grouped with the dispersed systems. The colloids are dispersed systems distinguished by the special value of their degree of dispersion. This view emphasizes, in other words, that there are no sharp differences between coarse suspensions, colloids and molecular dispersoids. We pass gradually from one into the other, and their properties change as smoothly. It is the purpose of today's lecture to prove the truth of this principle of continuity.

§1.

Let me first direct your attention to a further corollary to the conclusion that colloids represent dispersed systems in which the degree of dispersion has a special value. You have already seen how this modern definition compels the conclusion that every substance may appear in a colloid state, and how it systematizes also the general methods by which colloids may be prepared. The basis for a third conclusion may be introduced as follows.

I have here a coarse suspension of infusorial earth in water (demonstration). As you know, infusorial earth consists of the silicic acid coverings of minute organisms. There is no doubt, of course, that this mixture is one of *solid* particles in water. The same is true of this black precipitate of gold made by adding more gold chlorid and more reducing agent to the blue colloid gold I showed you yesterday (demonstration). The particles of gold in blue and red colloid gold must also be solid, for we cannot think of gold at ordinary temperatures as existing in any other form. *Coarse dispersions of solid particles in a liquid are known as suspensions; colloid dispersions of the one in the other, as suspension colloids or suspensoids.* In the terminology of P. EHRENBERG the latter are also known as *granular colloids.*

§2.

I show you in this flask two liquids which hardly mix with each other in molecular form, namely, water and benzol; I have added a little iodin to the latter to give it a violet color (demonstration). When I shake the flask you observe that I obtain mixtures of the one in the other, in other words, two emulsions, one of benzol in water and another of water in benzol. We have here divided two liquids into each other. As you know, this subdivision of two liquids into each other can be carried very much further, as seen in the milk of animals and plants, in cod liver oil emulsions, etc. The mixture may be so highly dispersed that high power microscopes are necessary to distinguish the separate droplets. This is true, for example, of human milk and of the milk of some rubber plants. Do we know emulsions of a colloid degree of dispersion? There are, of course, no reasons against the existence of such colloid emulsions or *emulsoids,* for we know that liquids dissolve in liquids and the principle of continuity underlying our classification of the dispersed systems clearly indicates that colloid emulsions must exist between the extremes of coarse dispersions and of molecular dispersions of one liquid in another. I show you here two types of such colloid emulsions or, to use the technical terms, of such emulsion colloids, emulsoids or *droplet colloids.* As an example of the first, I show you colloid sulphur (demonstration). As even the older investigators knew, droplets of liquid under-cooled sulphur are formed which slowly solidify or crystallize whenever sulphur is precipitated in watery solution. We have many reasons for believing that the microscopic and even colloid particles found in such mixtures retain this liquid form.[1]

In illustration of this second type of liquid-liquid colloids I could show you many examples, in fact, these are probably the best known and most widely distributed of all the colloids. Glue, gelatin, agar, protein, starch, rubber and collodion belong to this group. We shall discuss it in detail in the next lecture, when we shall also take up the differences existent, for example, between an emulsoid of sulphur and one of gelatin.

§3.

I have in this third flask an example of another coarsely dispersed system, a coarse dispersion of a gas in a liquid (demonstration). You see before you a saponin *foam.* There is no reason why a gas cannot assume a dispersed form. Are there dispersions of gases in liquid in which the degree of dispersion attains colloid dimensions? No doubt there are, for we are familiar both with coarse dispersions and with molecular dispersions of gases in liquids, but in illustration of them we can cite but few examples.[2] They are seen in the opalescent critical mixtures observed when liquids are evaporated, or gases are being liquefied in regions of critical temperature and pressure.

§4.

Certain objections may be raised to this *classification* of the colloids based on the state of aggregation of their constituents. The term itself, state of aggregation, refers to material in mass. It evidently loses its meaning as we approximate the molecular dispersoids in our progress through the series of dispersed systems. We cannot speak of the state of aggregation of a molecule. But how about colloid particles? May these still exhibit different states of aggregation? Our diagram of the dispersed systems and

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[1] See the monograph of S. ODÉN, Der kolloide Schwefel, Upsala, 1913.

[2] For some remarks regarding highly dispersed foams, see WOLFGANG OSTWALD, Kolloid-Zeitschr., **1,** 333 (1907).

our definition of the colloids show that we may still speak of the state of aggregation of colloid particles. The individual particles of a typical colloid must certainly consist of a whole series of molecules. As we reach the more highly dispersed among the colloids the properties peculiar to any given state of aggregation must gradually disappear. The properties of solid, liquid and gaseous particles must, in other words, become more and more alike. This is a necessary conclusion from the principle of continuity expressed in our diagram of the dispersed systems, for a molecular solution, for instance, of acetic acid in water, does not betray whether it was produced through the solution of solid, liquid or gaseous acetic acid in it. It is evident that we may expect to encounter interesting transition phenomena in this realm.

These remarks will serve to indicate how broad is the field of the colloids when the different states of aggregation and their possible combination into dispersed systems are considered. Thus far we have dealt only with the subdivision of a material in a liquid dispersion medium. But the dispersion medium might, of course, be solid or gaseous. When all this is borne in mind, the following eight combinations become possible in which the dispersed material or dispersed phase is named first, the dispersion medium second.

Solid + solid
Liquid + solid
Gas + solid

Solid + liquid (suspensoids)
Liquid + liquid (emulsoids)
Gas + liquid (foams)

Solid + gas (smoke)
Liquid + gas (fog)

It is important to emphasize that examples of coarse dispersions, of colloid dispersions and of molecular dispersions are known to us under all these different headings, although the coarse dispersions and the molecular dispersions are, for the most part, the more familiar examples.

Many of the minerals, the very important alloys, the solid solutions of van't Hoff, etc., belong to the system solid + solid. As colloid examples of the class, I show you some blue rock salt (colloid sodium in sodium chlorid) and ruby glass (colloid gold in glass). Examples of the subdivision of a liquid into a solid dispersion medium may also be found in mineralogy, as in the occlusion, inclusion and crystallization waters found in all degrees of dispersion in rocks. Systems illustrative of the type solid + gas are meerschaum, pumice, lava and solutions of gases in metals. Gaseous colloids with a solid dispersed phase are seen in tobacco smoke, cosmic dust, the vapors of ammonium chlorid, etc. Systems of the composition gas + liquid are seen in fogs of all kinds, as in the fogs about the earth, and in the clouds of the sky.

This list will, perhaps, impress you not only with the vastness of the general subject of the dispersed systems but with the extent to which these dispersions are of colloid dimensions. The modern concept of the colloid has served to bring together under one head many scattered elements. Where in the realms of physical chemistry could we formerly place the foams and the emulsions? These homeless and yet technically important structures are now not only properly cared for but are seen to be of the greatest significance in the science of colloid chemistry.

§5.

We come now to the main theme of today's lecture. We are to show that transition phenomena mark our passage from the coarse dispersions into the colloids, and from these into the molecular dispersoids. I shall combine with this a more detailed discussion of the physical and chemical properties of colloid systems. To this end I shall demonstrate the mechanical, optical, electrical and physico-chemical properties of some colloid solutions while showing you at the same time how these change as we pass through the different degrees of dispersion. Today's subject might be called *the physico-chemical properties of dispersed systems and their variation with the degree of dispersion.*

Let us first consider some of the mechanical properties of dispersed systems. If you examine microscopically a fine suspension of carmine particles in distilled water, you observe that the particles are in a state of spontaneous movement; they dance and rotate in an apparently irregular manner, the individual particles following such paths as have been plotted in Fig. 19.[1] These movements are not induced through an expenditure of light or heat energy nor are they dependent upon electrical or chemical changes. Moreover, all known dispersed systems show this so-called Brownian movement whenever two conditions are satisfied. First, the dispersed particles must be sufficiently small. As a rule Brownian movement does not manifest itself clearly until the particles have a diameter of 0.5 μ or less. Second, the dispersion medium must be sufficiently mobile to permit the movement. The movements could not appear in solid glass, for instance. But if these two conditions are satisfied, all dispersed systems show Brownian movement. It is observed, for example, in milk, in gas bubbles and very beautifully in smoke. It seems, therefore, to be a general property of dispersed systems and under constant conditions is apparently everlasting. Brownian movement is observed in the liquid inclusions found in minerals which are certainly thousands of years old.

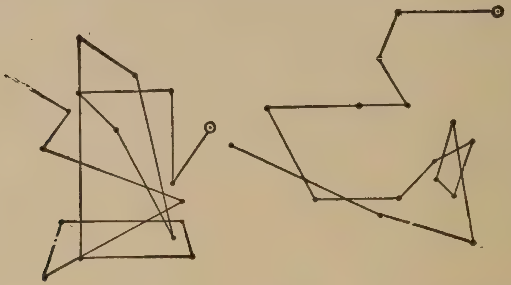

Fig. 19.—"Paths" of two particles in Brownian motion.

How does this Brownian movement change with changes in the degree of dispersion? Do we observe a Brownian or similar movement in colloids and in molecular solutions?

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[1] I was in the habit of concluding the lecture by demonstrating ultramicroscopic apparatus and with this, Brownian movement.

I have already told you that Brownian movement of microscopically visible particles is observed only when these are highly dispersed. The intensity of the movement increases markedly as the microscopic particles decrease in size. Our concept of continuity would lead us to conclude that such movement must appear in colloids and molecular solutions also, and since the degree of dispersion is greater, the movement would occur much more rapidly here than in microscopic dispersions. There no doubt now comes to your mind the old and much-discussed belief that in all molecular systems, as in gases and liquids, the molecules are in a state of marked, even tumultuous, activity. The famous kinetic theory of gases and liquids is built upon this fundamental assumption. It can be shown by optical methods, which we shall discuss later, that spontaneous movement not only occurs in colloids, but is more intense in them than in microscopic dispersions. It has been possible to show that this greater velocity of Brownian movement approximates the values calculated for the speed of molecules. Conversely, the laws which have been formulated for the kinetic movement of molecules hold also for the Brownian movement of colloids and coarse dispersions if their degree of dispersion is duly considered. We shall return to this subject when we come to discuss the scientific applications of colloid chemistry. No physical chemist today questions the correctness of the statement that this "spontaneous internal movement" is common to all dispersoids and that its intensity increases steadily as we pass from the coarse dispersions, on the one hand, through the colloids, to the molecular solutions on the other.

§6.

Let us now consider another mechanical property of dispersed systems. A particularly important qualitative characteristic of colloid solutions is their failure to diffuse and to dialyze. Typical colloids do not diffuse any more than do coarse dispersions. Are there transition systems which occupy a position between the colloid and the molecular systems, or — and this would be a particularly pretty proof — can we make one and the same substance appear at one time in diffusible and at another in non-diffusible form? An experimental answer can be given to both these questions. We know many solutions which assume this intermediate position so far as diffusion is concerned. Many proteins, ferments, toxins, antitoxins and dyes, such as congo red, night blue, etc., show a hardly measurable but nevertheless definite diffusibility. Slight changes in the dispersion media suffice at times to impart to these transition systems a well-marked diffusibility. Thus certain albumins do not diffuse into distilled water but diffuse readily into dilute salt solutions. The neutral salts dehydrate the heavily hydrated colloid albumin particles, thereby increasing their dispersion and so their diffusibility.[1] All degrees of diffusibility are encountered in passing from the molecularly dispersed to the colloid solutions.

But even one and the same substance in a given dispersion medium without any additions from the outside, may either diffuse or not, depending upon its degree of dispersion.

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[1] Papers dealing with this subject hardly discuss the fact that the addition of a neutral salt or of alcohol to a hydrated colloid may bring about two totally different, antagonistic effects. First, addition of these foreign materials *increases* the degree of dispersion by dehydrating the particles; through secondary agglomeration of the particles there then occurs a *decrease* in degree of dispersion which may end in coagulation. According to unpublished experiments of my own, this double effect is separable by proper methods, and explains, for example, the formerly unintelligible fact that protein solutions diffuse more readily into dilute salt solutions than into distilled water. See WOLFGANG OSTWALD, Handbook of Colloid Chemistry, translated by FISCHER, second English edition, 227, Philadelphia, 1919. It also explains why colloid dyes like congo red upon the addition of salts first turn towards yellow and only later, shortly before precipitation, towards violet. The fact that large amounts of neutral salt must be present to accomplish the crystallization of proteins is also to be explained by the influence of the neutral salts in bringing about a decrease in the degree of dispersion of the hydrated colloid. It is presumable that the crystalline or vectorial forces of the particles will come into action best when the amount of indifferent solution medium bound to the particles and tending to inhibit their coalescence, is least.

This was proved years ago by W. RAMSAY'S pupils, H. PICTON and S. E. LINDER, for the precipitates of arsenic trisulphid. In keeping with the law of VON WEIMARN these authors obtained, from very dilute solutions, precipitates of arsenic trisulphid which were not only invisible under the microscope and passed a filter, but showed undoubted diffusibility. Similar observations, according to my experience, may be made on the highly dispersed colloids of berlin blue and according to THE SVEDBERG on colloids of gold. In fact, in gold the connection between degree of dispersion and diffusibility seems so simple that the diffusion coefficient appears as inversely proportional to the diameter of the particles.[1] This constitutes, moreover, a quantitative conclusion derived from application of the kinetic theory to these more coarsely dispersed systems. All these facts leave no room to doubt that diffusibility and therefore dialyzability increase *progressively* as the degree of dispersion increases, just as in BROWNIAN movement.

§7.

If we would discover examples of transition phenomena in the mechanical properties of coarse dispersions and of colloids we may study their behavior during filtration. We may recognize different degrees of dispersion as they will or will not pass through filters of a known porosity. To give you some idea of the estimated size of the pores in different filters, I show you the following table.

SIZE OF PORES IN FILTERS

Filter paper No. 1450 (Schleicher and Schüll)	About 4.8 μ
Filter paper No. 598 (Schleicher and Schüll)	About 3.3 μ.
Ordinary thick filter paper	About 3.3 μ.
Filter paper No. 597 (Schleicher and Schüll)	About 2.9 μ.
Filter paper No. 602 hard (Schleicher and Schüll)	About 2.2 μ
Filter paper No. 566 (Schleicher and Schüll)	About 1.7 μ.
Filter paper No. 602 extra hard (Schleicher and Schüll)	About 1.5 μ.
Chamberland filter	About 0.2 to 0.4 μ.
Reichel filter	About 0.16 to 0.18 μ.

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[1] See THE SVEDBERG, Zeitschr. f. physikal. Chem., **67**, 105 (1909).

In keeping with our definition, colloids would, therefore, be held back only by the fine porcelain filters.

C. J. MARTIN, G. MALFITANO, H. BECHHOLD, and others have, however, taught us how to make filters which enable us to separate colloids from their dispersion media. We shall soon see, as a matter of fact, that filters may be prepared which will, in part at least, bring about a mechanical separation of dispersed phase from solvent even in the case of the molecular dispersoids. Such denser filtration media are found in different organic and inorganic *gels*. If ordinary filter paper, for example, is impregnated with collodion by the simple method which I have described,[1] these *colloid or ultrafilters* may be used to separate the dispersed phase of colloid solutions from the dispersion medium just as the materials of a coarser suspension may be separated from the "solvent" with an ordinary filter. Let me pour into a "spontaneous" ultrafilter thus made, a dilute solution of night blue, India ink, blue colloid gold, or a colophonium hydrosol (demonstration). As you observe there drips through only the colorless dispersion medium. In order to prove that the original highly colored fluids are really colloid solutions and not coarsely dispersed systems I have set up a series of ordinary filters. As you see the different fluids

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[1] Regarding simple ultrafilters see WOLFGANG OSTWALD: Kolloid-Zeitschr., **22,** 72, 143 (1918); Kleines Praktikum der Kolloidchemie, 24, Dresden, 1920. The following recipe is a satisfactory one for the production of ultrafilters which filter "spontaneously," in other words, under simple hydrostatic pressure. They are well adapted to demonstration purposes. A sheet of ordinary, smooth filter paper is fitted closely into a clean funnel and saturated with water, any excess of water being shaken out. Twenty to thirty cc. of a carefully warmed collodion solution (4 percent) are poured into the *moist* filter. A first collodion layer (the so-called "spongy" layer) is produced by turning the funnel about and allowing the collodion to spread evenly over the paper. Any excess is carefully poured away, care being taken that no drop remains in the tip of the filter. The whole arrangement is permitted to dry in the air some five to ten minutes during which time the stiffening filter is taken out of the funnel now and then. The collodion solution is poured a second time into the filter to produce a second layer, any excess of the solution being again carefully gotten rid of. After five to ten minutes of drying in the air the filter is submerged in distilled water. After remaining in this for about one-half hour it is ready for use.

run through these in colored or turbid form. The systems being filtered are therefore really colloid systems. In order to hasten ultrafiltration or to make filtration possible through still denser media the filters may be mounted in a suction flask (Fig. 20) and connected with a water pump; and to obtain larger filtration surfaces porcelain funnels may be used. I have on the table several styles of such ultrafilters, useful for various purposes. We can so vary the permeability of the ultrafilters through the addition of various substances or by changing their concentration that from a given colloid we may obtain fractions differing from each other in the degree of their dispersion. Concentrated gels hold back even the most highly dispersed colloids. If we use inorganic gels of the type of berlin blue made by mixing together highly concentrated solutions, we obtain the so-called *semipermeable membranes* used in osmotic experiments. These jelly-like precipitates may be so impermeable, as in the case of copper ferrocyanid, that they will not give passage even to many dissolved molecules. We can make use of this property not only to bring about changes in the concentration of molecular solutions in which the osmotic pressure assumes the rôle of filtration pressure, but to bring about a separation of the solid salt in highly concentrated solutions. Thus, according to the physiologist C. LUDWIG, a fairly concentrated solution of sodium sulphate begins to crystallize when a piece of dried pig's bladder is introduced into it, for only water and not salt diffuses into this concentrated gel. All this again serves to show that we pass by easy steps from ordinary filtration through ultrafiltration to osmotic or "superultrafiltration" (P. P. VON WEIMARN).

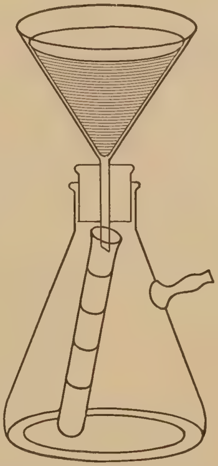

FIG. 20. — Simple arrangement for ultrafiltration.

§8.

When we consider the *optical* properties of colloid systems we again encounter a large number of beautiful and interesting transition phenomena. Perhaps the most general optical phenomenon encountered in dispersoids is that of optical heterogeneity, or turbidity. A dispersed material and the dispersion medium will ordinarily hardly be expected to show the same coefficient of refraction. A ray of light passing through the system will, therefore, not be able to do so undisturbed. This is the scientific explanation of turbidity, so well shown by coarse and microscopic dispersions of all kinds. I need but remind you of the white color of quartz suspensions, of milk and of foam. But a large number of colloids also appear turbid if properly studied, as these colloid metallic sulphids, this bluish-black colloid gold, etc.

We can best perceive slight turbidities by viewing a solution against a black background, in other words, by light coming chiefly from one side. How much unilateral lighting aids us in recognizing slight turbidities is familiar to you from observing dust particles in a ray of sunlight. When a pencil of bright light is thrown into a darkened room we not only see the bright cone but in it a large number of dust particles which escaped us when the light came from all sides. This method of demonstrating fine turbidities was used even by FARADAY to prove the disperse nature of solutions of colloid gold. In this way he demonstrated the disperse nature of red gold which ordinarily seems entirely clear. The method was used in more extensive fashion by J. TYNDALL, in whose honor we call the light cone observed in dispersoids when illuminated from one side only, the TYNDALL cone.

The majority of all typical colloids shows a Tyndall cone. Since this is a matter of much interest I shall demonstrate it to you (demonstration).

We have here an arc light from which we obtain a narrow pencil of light which passes into this vessel with parallel sides filled with distilled water. You observe, I hope, nothing but a slight glow in the water. If the water were absolutely pure, if it did not contain even the slightest traces of dust or air, and were I able to shut out all reflection from the walls of the vessel, you would see nothing at all. It is experimentally possible to produce water which to the naked eye is thus "optically empty." Let me now pour into this vessel a few cubic centimeters of a brown solution of colloid silver, which as you saw before, is also perfectly clear to the naked eye. As the two liquids mix, an intense greenish-white cone of light flashes into view (Fig. 21). This is the famous Tyndall cone and is due to the optical heterogeneity of colloid solutions.

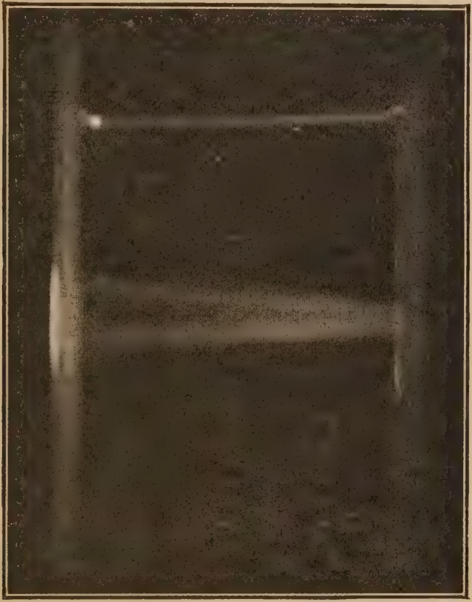

Fig. 21. — A Tyndall cone.

I could take up one after the other of the colloid solutions on the table and in almost every one of them show you this Tyndall effect.

There are, of course, colloids which show it but little, such as blood serum,[1] alkali albuminates, freshly prepared silicic acid and very pure congo red solutions. These colloids belong to that second class of emulsoids to which I have already called your attention and which we shall discuss in detail in the next lecture. These colloids are characterized by their great *hydration* or *solvation.* Their particles have taken up a large amount of the dispersion media; in fact, they may at times consist chiefly of this. This explains why such colloids show the TYNDALL effect but weakly. To change the direction of a light ray it is necessary that a distinct refraction difference exist between dispersed phase and dispersion medium. But if the colloid particles are largely built up of the dispersion medium itself, the optical difference between combined and uncombined dispersion medium is but slight. This is why typical colloids and even coarse dispersions do not necessarily appear turbid. Coarsely dispersed powdered glass in Canada balsam of the same coefficient of refraction, for instance, does not appear turbid. One must be careful, therefore, to avoid the common mistake of concluding that a material is highly dispersed just because it is not turbid.[2]

§9.

To what degree of dispersion may a material be carried and still show this TYNDALL phenomenon? And what changes does it show as we pass over into the field of molecularly dispersed solutions? In order to answer these questions we must enter, for a moment, upon the theory of these turbidities. As we ascend the dispersion scale, optical heterogeneity becomes attributable more and more to

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[1] According to F. BOTTAZZI fresh blood serum is practically clear optically; see WINTERSTEIN, Handbuch der vergleichenden Physiologie, **1,** 145.

[2] A silicic acid solution showing practically no TYNDALL phenomenon has been observed by C. O. WEBER, Chemistry of India Rubber, 3rd edition, 74, London, 1909.

optical causes other than the mere lateral deviation of light rays observed in coarsely dispersed systems. While in the latter the turbidness is chiefly attributable to refraction, that in the most highly dispersed systems is due to diffraction. When the diameter of the dispersed particles falls below that of the length of the light waves illuminating them, refraction in the ordinary sense of the word can no longer take place. Instead, a diffuse dispersion of the light in all directions takes place. This occurs even in colloids, for colloid particles have already a diameter of but half a wave length or less. The TYNDALL phenomenon as observed in colloid solutions is therefore really due to light dispersion. It follows from the nature of this dispersion that when mixed light is used the shorter rays are bent *more* than the longer ones. The blue, violet and ultraviolet rays of a TYNDALL cone will, therefore, be bent more than the yellow and red rays. This results in that play of colors known as opalescence, to which we shall return in a moment. Furthermore, it is clear that the short waves will still be bent by particles too small to bend, for instance, the blue, yellow or red rays. This is a matter of much interest to us. When the TYNDALL method is so refined that we are enabled to perceive not only mixed blue or violet light but ultraviolet light, then *it becomes theoretically possible to recognize a turbidity even in molecularly dispersed systems.* Just as colloid particles may interfere with the longer waves of visible light, molecules may effect a disturbance in the shorter ultraviolet rays.[1] One way of refining the TYNDALL method is to employ photography, which you know to be particularly effective in proving the presence of the chemically active ultraviolet rays. I have myself observed that distilled water which is optically clear to the naked eye shows a marked TYNDALL cone photographically. But this is lost on interposing between water and camera a thick glass plate

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[1] Regarding TYNDALL cones due to ultraviolet and even shorter light waves, see WOLFGANG OSTWALD, Koll.-Zeitschr., **13**, 121 (1913).

which absorbs most of the ultraviolet rays. By employing ultraviolet TYNDALL cones, a number of investigators have recently been able to demonstrate by photographic methods the existence of turbidities in systems of various kinds[1] not directly discernible by the senses.

But how about experimental proofs of the existence of such extremely fine turbidities in the transition systems between colloids and molecularly dispersed solutions; or of their existence in the latter? It is self-evident that experiments to this end belong to the most delicate in the whole realm of physical optics. First to be considered is the presence of impurities, the presence, in other words, of "optical dust," in the liquids to be examined which tends to enter every time that they are manipulated and which explains, for example, the paradoxical finding that the amount of such optical dust is often increased instead of diminished through filtration, distillation, etc. The Belgian investigator, W. SPRING, has devised ingenious methods to clear such systems of optical dust and has observed the purified liquids to be optically clear when observed directly. But photographic study of these liquids by M. LE BLANC and W. KANGRO still showed the plates to be affected, — there still existed, in other words, delicate optical impurities. Furthermore, W. SPRING, LOBRY DE BRUYN and others have shown that *many of the molecularly dispersed solutions, like concentrated cane sugar, cannot be made optically clear by any method whatsoever, in contrast to other molecularly dispersed systems which, after purification by similar methods, no longer show subjectively a Tyndall cone.* Evidently, there exist here the transition phenomena which

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[1] This greater sensitiveness of a TYNDALL cone to photography probably explains the discrepancies between the studies of W. KANGRO [Zeitschr. f. physik. Chem., **87,** 257 (1914)] and W. SPRING. While the latter succeeded in obtaining water and various salt solutions in a form optically empty to the human eye — a possibility which every microscopist is able to corroborate — the former could confirm these negative findings of SPRING only in part when he used photographic methods.

interest us, for a concentrated cane sugar solution shows itself by other methods to approximate a colloid solution.[1] P. WOLSKI working in the Physico-Chemical Institute of the University of Leipzig[2] has lately prepared, by methods of ultrafiltration employed in the absence of air and under otherwise extremely delicate laboratory conditions, concentrated cane sugar solutions *which in a thickness of 45 μ showed no* TYNDALL *cone subjectively.* But this does not yet prove that turbidities are non-existent in molecularly dispersed systems. Liquid sheets so thin (45 μ = 0.045 mm.) might be clear while thicker ones might show a turbidity, especially if investigated by indirect, for example, photographic methods.

A striking example which illustrates the importance of the thickness of the layer in bringing about a turbidity is furnished by the earth's atmosphere. No one, under a blue sky and upon a mountain top, would consider air a turbid medium or would be able to demonstrate a turbidness in a layer 1/500 of a millimeter thick. And yet the purest air when viewed in its entire thickness shows the optical properties of a turbid medium — properties which interestingly enough are attributed by LORD RAYLEIGH and other physicists, not to the presence of dust and water particles, but to the dispersing effects of the air molecules themselves. The famous Polish investigator M. VON SMOLUCHOWSKI has, as a matter of fact, observed that carefully purified air shows a slight TYNDALL phenomenon even in laboratory experiments, — a turbidity which he, too, declares molecular.[3] We are face to face here with compli-

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[1] A discussion of transition phenomena as observable in concentrated cane sugar solutions may be found in WOLFGANG OSTWALD and K. MÜNDLER, Koll.-Zeitschr., **24,** 11 (1919).

[2] See M. LE BLANC and P. WOLSKI, Ber. d. sächs. Ak. d. Wiss., **72,** 24 (1920); P. WOLSKI, Kolloidchem. Beihefte, **13,** 137 (1920).

[3] M. VON SMOLUCHOWSKI, Bull. Acad. Cracowie, 218 (1916); R. FÜRTH, Schwankungserscheinungen in der Physik, Vieweg'sche Samml., No. 48, 61 (1920).

cated questions. Not only the presence of impurities but the methods used, the thickness of the layer, the intensity of the illumination — all these and other factors need to be considered when we try to say that molecularly dispersed systems are turbid or not. At the present time we can only say that facts,[1] exist which suggest that pure, molecularly dispersed systems may show an optical heterogeneity especially when observed in thick layers and with light of short wave length but that conclusive proof is difficult. Our concept of continuity, however, convinces us that such experimental proof will some day be forthcoming.

This concept of continuity leads us further.[2] It is clear that we may employ rays even shorter than those of ordinary light of the ultraviolet light to prove the existence of

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[1] The optically clear, concentrated solutions of cane sugar, citric acid, etc., prepared by P. Wolski show a property which is never observed in dilute solutions or water, and one which speaks strongly for an optical heterogeneity in these systems. When dust particles, purposely introduced into these solutions, are observed ultramicroscopically they are found to be surrounded by a remarkably large bluish-white field of light which is never observed in water, for example, and which is so intense that it often lights up a large part of the whole visual field. One is inclined to attribute the fact to a "secondary Tyndall effect" in which the source of light is derived from that reflected by the dust particles.

[2] Wolfgang Ostwald, Koll.-Zeitschr., **13,** 121 (1913) from which I quote: "This refraction of Röntgen rays should be used not only for the study of the symmetrically arranged discontinuities observable in crystals (as has been done by M. Laue and his co-workers) but for the analysis of the irregularly arranged or diffuse refractions observable, for example, in homogeneous liquids, molecular solutions, etc. It will broaden our knowledge of turbidity and of radiation effects in dispersed systems when this method is used and will develop knowledge beyond that now obtainable through the use of ultraviolet light. A Röntgen 'Tyndall cone' would make accessible to optical investigation degrees of dispersion lying beyond the reach of the normal Tyndall cone and the ultraviolet Tyndall cone, the microscope and the ultramicroscope. It would be of interest if this question were investigated experimentally." The remarkable work by P. Debye and W. Scherrer who have actually used this idea in their study of benzene, no doubt without knowledge of the above remarks, did not appear in the Physikalische Zeitschrift until 1916.

fine optical heterogeneities, for example, Röntgen rays, which are but 0.04 to 0.06 $\mu\mu$ long and which, according to the observations of C. Barkla and others, can also be deviated from their course. For the solution of this problem the investigations of M. Laue, the two Braggs, P. Debye and their co-workers are important, who succeeded in photographing the refraction pictures of Röntgen rays passed through crystals and in this way obtained pictures consisting of tiny spots of light arranged in a manner and at distances from each other which in large measure corresponded with the arrangement of the *atoms* in the crystal. Each of the spots upon the photographic plate was made by a concentrated pencil of Röntgen rays and showed an intensity dependent upon the spacial orientation of the molecules in the crystal.[1] Even when Röntgen rays are passed through "homogeneous" liquids like benzene P. Debye and W. Scherrer observed diffraction phenomena permitting of deductions regarding the size and shape of the benzene molecule. There is therefore in this region of the highly dispersed systems also striking agreement between theoretical deduction and experimental finding.

One can hardly imagine a more perfect and continuous series of phenomena for proving the continuity of the different classes of dispersed systems than that represented by the microscopic turbidity of coarsely dispersed systems, the visible Tyndall cone of typical colloids and concentrated molecular dispersoids, the invisible ultraviolet Tyndall cone, and finally the Röntgen ray Tyndall cone of systems alleged to be homogeneous.

§10.

Permit me to return for a moment to the Tyndall phenomenon as observed in typical colloids. It is of much

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[1] For details, see, for example, the collective presentation of F. Rinne, Die Naturwissenschaften, Nos. 17 and 18 (1916); No. 4 (1917).

interest, for it illustrates a principle of great importance in the analytical methods of modern colloid chemistry. As you know, when observing dust in the sun, we occasionally see particles become visible temporarily which are so small that we miss them ordinarily. If we watch closely, we note that these particles are surrounded by a luminous ring or halo similar to that observed along the edges of an opaque object when viewed against the setting sun. As the object viewed against the light becomes smaller, its edges become contracted and the visual image no longer corresponds accurately to the geometrical figure. When the particles become sufficiently small, the figure disappears entirely and its place is taken by a single luminous point. Similar phenomena are observed under the microscope when we use dark ground illumination. The arrangement corresponds to a viewing of the TYNDALL phenomenon against a dark background. It is important to remember that particles will show this diffraction phenomenon even when smaller than a wave length of light. The limits of ordinary microscopic visibility, or, to put it more accurately, the limits for obtaining a correct geometrical picture are set, as I told you, by the length of the light waves. We can still, however, obtain diffraction pictures or diffraction spots of particles which are smaller than the length of a light wave.

This method of demonstrating optically the presence of individual particles *less* than a wave length in diameter, by utilizing the principles of diffraction, but with sacrifice of the geometrical image, we call ultramicroscopy. Since colloids are by definition dispersed systems in which the dispersed particles have a diameter of less than a light wave, they may be rendered visible by using dark ground illumination. *This was accomplished for the first time by the two German investigators*, H. SIEDENTOPF and R. ZSIGMONDY, to whom we are also indebted for important developments in ultramicroscopic methods. The importance of ultramicroscopic methods in rendering visible the individual particles in colloid systems and in thus proving the gradual transition of coarsely dispersed particles to those of colloid dimensions is self-evident.

You obtain a good idea of the principles of ultramicroscopy if you imagine yourself looking at a TYNDALL cone with a lens or a microscope. The Belgian investigator W. SPRING many years ago used a magnifying glass on TYNDALL cones and the beginning of our present day ultramicroscopy may be seen in the arrangements for dark ground illumination so long used by bacteriologists and students of diatoms. We can, of course, use high powers of the microscope to accomplish the optical analysis of a TYNDALL cone. The brightest spot of a small TYNDALL cone is then thrown just below the objective of a microscope, as shown in Fig. 22. It would take us too far afield were I to discuss the details of construction of ultramicroscopes or to tell you of the many observations that have been made with them. I shall only point out that such suspensoids as the colloid solutions of the metals yield varied and often extraordinarily colored ultramicroscopic pictures. The TYNDALL cone produced by a solution of colloid gold is filled with innumerable brilliant

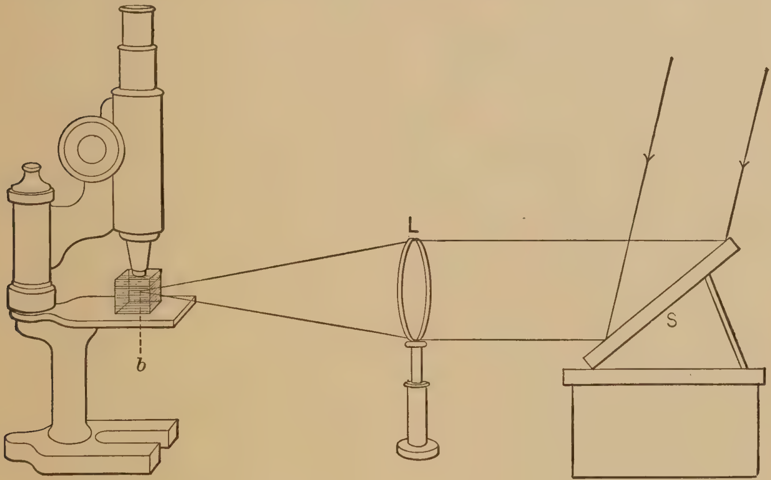

FIG. 22.—A simple arrangement for ultramicroscopy according to R. ZSIGMONDY.

points showing beautiful Brownian movement. On the other hand, such things as proteins and certain dyes do not analyze into "ultramicrons." This is not always because the particles are too small but because, as previously stated, they are so highly hydrated that their coefficient of refraction is not very different from that of their dispersion media.[1] These facts can be better demonstrated than described and so I must ask you to wait for the experiment which I shall present at the end of this lecture.[2] What, now, are the limits of visibility of particles ultramicroscopically? This question is of interest in connection with our concept of continuity. Suffice it to say that such limits are in high degree dependent upon the intensity of the illumination. By using light from an arc or from the sun we may still establish the existence of particles having a diameter of a few millimicrons. Of course the photochemical effects of the light are often so intense in such investigations that they are carried out with great difficulty.

In connection with our concept of continuity, it is a matter of importance that R. Zsigmondy was able to produce rose colored colloids of gold which were so highly dispersed that they could not be analyzed under the ultramicroscope even when direct sunlight was used, a behavior in keeping with the previously discussed fact that these colloids show also a distinct tendency to diffuse.

§11.

Of much interest is the color of colloid systems. One of the simplest of the questions under this heading is that of their *opalescence*, or, differently expressed, the "color of the

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[1] This mistake of concluding from negative ultramicroscopic findings that the material in hand is therefore necessarily a molecularly dispersed one is still made.

[2] I was in the habit of demonstrating at the end of this lecture such ultramicroscopic apparatus as circumstance provided, the nature of the demonstration being determined by the number in the audience and its interest. For a detailed description of ultramicroscopic pictures, the reader is referred to the text-books of colloid chemistry.

colorless colloids." All sorts of solid, liquid and gaseous colloids are bluish or violet when viewed against a dark background; or yellow and red when we look through them. You need but look at these solutions of gelatin or albumin, at this colloid mastic (prepared by pouring an alcoholic solution of mastic into water), at this milk glass, and at this white opal[1] (demonstration). The greatest example of a gaseous dispersoid exhibiting opalescence is seen in the sky. When we look at a cloudless sky against the dark background of space, this heavenly dispersoid looks blue; but when we look through it against a source of light (as against the sun when it is coming up or going down) we find it yellow or red. The cause of this opalescence is to be found in the fact that the longer yellow and red rays are less disturbed and bent in a highly dispersed system than are the shorter violet and blue rays.

To show you that not only yellow and blue colors may appear in dispersed systems composed of two substances in themselves colorless, I present this flask of polymerized cinnamic ethyl ester. You note a beautiful greenish-red opalescence which would give way to a bluish-yellow were I to warm the mixture. The system consists, as shown on TYNDALL analysis, of a mixture of monomolecular ester and polymerized ester of which the particles have attained at least colloid dimensions. You may note similar color phenomena in the gelatinous colloid sodium chlorid previously shown you. In fact, you may observe such CHRISTIANSEN opalescence when you merely powder sodium chlorid very finely and suspend it in a mixture of benzol and carbon disulphid of practically the same coefficient of refraction as the sodium chlorid itself. It would take us too far afield to enter into the theory of these interesting phenomena.[2]

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[1] The play of colors in the opal is due in part only to opalescence, in part to the interference colors produced by thin plates.

[2] A detailed discussion of these CHRISTIANSEN colors and of related problems will be found in a volume entitled, Light and Color in Colloids, which I hope to be able to publish soon.

Opalescence also varies greatly with the degree of dispersion. Coarsely dispersed systems are but slightly opalescent, while colloid systems are intensely so. So far as the opalescence of molecular dispersoids is concerned, we find that some investigators, like LORD RAYLEIGH, assume that opalescence may still be produced through the disturbing effects of molecules. This is the case, for example, in certain gases, and it is held that at least a part of the opalescence of the sky may be dependent upon such a selective bending of light rays by the molecules of the atmosphere. Even when we grant this molecular opalescence, the fact remains that its *intensity* decreases as we pass from the colloid into the molecular region. This is amply illustrated by the fact that most salt solutions and most gases are colorless unless viewed in enormous thicknesses, as presented by great masses of water or in the earth's atmosphere.

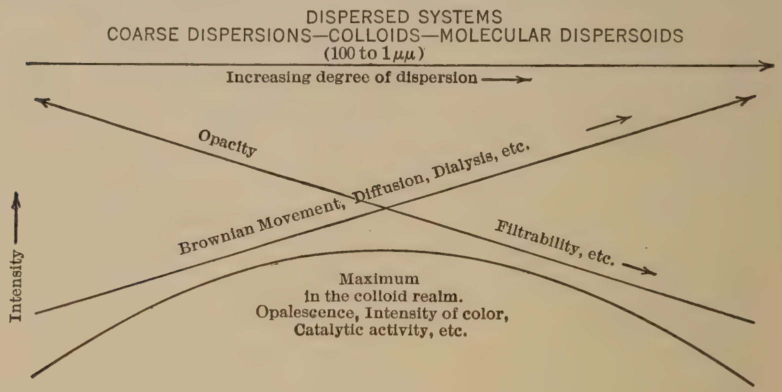

FIG. 23.

We note in this discussion a first illustration of the fact that the intensity of a property of dispersed systems may show a *maximum*, and this in the colloid realm. Previously we have only dealt with properties which either increased steadily with increase in degree of dispersion (as BROWNIAN movement and diffusion velocity) or such as decreased steadily (as the phenomena of heterogeneity) as we passed from coarse dispersions through colloids to molecular dispersions. As we proceed, we shall find further illustrations of how certain properties of dispersoids may show a maximum or minimum in the colloid realm, as indicated in Fig. 23.

§12.

The next property to be discussed, that of the *intensity* of color in colloid solutions, illustrates this. As is well known, such colloid salts of the metals as the sulphids may show so marked a color even in very low concentrations that it may be used for their qualitative recognition. The coloration intensity of these colloids may at times be greater even than that of the aniline dyes. Thus if the coloring intensity of fuchsin is represented by the arbitrary value of 5, that of colloid iron hydroxid is about the same, while that of arsenic trisulphid is 100, and that of colloid gold about 2000 (The Svedberg). When the coloration intensity of a substance in different degrees of dispersion is studied, it is found to *attain a maximum in the realm of colloid dispersion.*

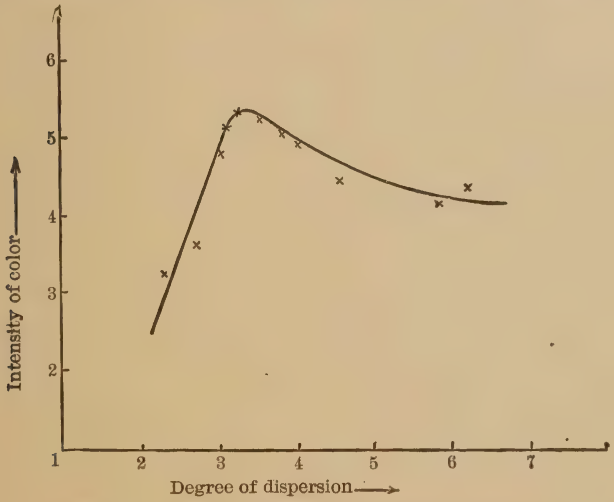

Fig. 24.—Relation of color intensity of colloid gold to its degree of dispersion according to The Svedberg.

If we choose gold as an example, it is easily seen that a black, coarsely dispersed gold precipitate has less covering power than a solution of gold containing the same amount of metal in colloid form. When colloid gold is coagulated or precipitated, the solution becomes "decolorized." The small amount of black precipitate which falls to the bottom of the flask has again a minimal covering power. You will perhaps recall that in preparing colloid gold I started with a gold chlorid solution which was practically colorless; in other words, one which hardly showed the yellowish-brown color of the ion. From this colorless solution we obtained the intensely red and blue gold colloids. It is therefore certain that colloid gold has a more intense color than either coarsely or molecularly or ionically dispersed gold; in other words, a maximum is observed in the colloid realm. The accompanying Fig. 24, taken from THE SVEDBERG, illustrates quantitatively the appearance of this color maximum in the colloid region.

§13.

Not only is the intensity of colloid colors a noticeable fact, but their beauty and *variety* as well. I have already shown you red and blue gold, and by precipitating this metal with oxalic acid we can obtain green gold. Silver and platinum in the colloid state also show many different colors. Gold, silver and platinum may therefore be regarded as panchromatic.

I have here a number of photographic plates prepared by LÜPPO-CRAMER'S methods, which show differently colored silver colloids in gelatin (demonstration).[1] These were, as a matter of fact, made by his own hands. You observe that the plates are yellow, orange, red, violet and blue; and here I show you one that is green. When you first look at this plate it is greenish violet, but I need only dip it in water for a few seconds for you to see this color give

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[1] These preparations were kindly given me by Drs. LÜPPO-CRAMER and R. E. LIESEGANG. I should like here also to thank them for their kindness.

way to a clear dark green (demonstration).[1] All these colors are the colors of colloid silver and one naturally asks why they differ so. Let me point out that we are again indebted to an American for a first study of this question. Carey Lea recognized and investigated the colors of colloid silver and gold many years ago.

The different colors of one and the same metal in a colloid state are chiefly referable to *differences in their degree of dispersion.* There is, of course, much room for differences in degree of dispersion even within the realm of the colloid dimensions themselves which lie between 100 and 1 $\mu\mu$, and it is in these finer differences that the explanation of the color changes must be sought. To prove this, I need but add some barium chlorid to this red colloid gold, and stir the mixture (demonstration). The salt coagulates the gold; in other words, it changes the gold to a coarsely dispersed precipitate. A first effect is a *change in color.* As you see, the mixture becomes violet. In a little while it will turn blue and then gradually become greyish black.[2] The different colors of silver which I showed you are also to be explained through such differences in the sizes of the metallic particles, dependent upon the methods used in their preparation.

The *order* in which the colors change from one to the other as the degree of dispersion changes seems also to be definite. As a rule, the most highly dispersed colloid metals are yellow or orange; in other words, they absorb violet and blue light. As the degree of dispersion decreases, the color passes from yellow through orange to red, violet, blue and finally green. The absorption maximum gradually moves toward the side of the greater wave

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[1] See Lüppo-Cramer, Koll.-Zeitschr., **8**, 240 (1911).

[2] These experiments are best made with large quantities of the red colloid gold [alcohol-gold, Wolfgang Ostwald, Kleines Praktikum der Kolloidchemie, 2, Dresden, 1920] contained in two cylinders. Not too much of the barium chlorid must be added at once, otherwise precipitation in coarse form occurs immediately without the change to the blue color being clearly visible.

lengths as the degree of dispersion decreases.[1] The same order is frequently observed in organic dyestuffs when the colors of any homologous series are studied. Yellow is usually the color of the chemically simpler members, while the dyes of greater molecular complexity in the same series are often blue and violet.

I am indebted to my pupil R. AUERBACH[2] for a beautiful example of this relation between color and degree of dispersion. This parallel-walled glass container illuminated from one side by the intense beam of light from a projection lamp contains a dilute solution of sodium thiosulphate (demonstration). I will add to it a few cubic centimeters of a dilute solution of phosphoric acid. As you know, the salt is decomposed by the acid with the liberation of sulphur. At the concentrations employed the sulphur separates off in particles of colloid size. The particles will, however, grow gradually until a thick, milk-like mixture is obtained containing coarsely dispersed sulphur. *During* this gradual growth the system shows a surprisingly clear and beautiful series of different colors. Upon looking through the vessel the mixture is at first yellow but it soon changes to orange. If we wait a little while we will note a change to red. Later the mixture will become violet and then a beautiful and striking blue, passing, at times, to a blue-green. The color is then likely to fade, the system becoming non-transparent or "gray." Please note that in the sulphur of this experiment we are dealing with a dielectric substance and that the changes in color observed obey the general law of relation of color to size of particle.

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[1] For further details regarding this relation between color and degree of dispersion, see WOLFGANG OSTWALD, Kolloidchem. Beih., **2,** 409 (1911), as well as my forthcoming monograph, Light and Color in Colloids.

[2] See R. AUERBACH, Polychromie des Schwefels, Koll.-Zeitschr., **26,** 239 (1920). — A mixture, well suited to projection purposes, is the following: 15 cc. 0.05 $Na_2S_2O_3$ + [0.1 cc. H_3PO_4 (of a density of 1.70) + 4.9 cc. H_2O]. The whole run of colors from yellow to blue-green occurs within about 20 minutes. The thickness of the fluid should be about 1 cm.; the illumination as intense as possible.

Our illustration is also interesting because no "foreign" electrolyte was added so that all the changes observed can only have been due to the "spontaneous" increase in the size of the particles during their precipitation.

What about *transition phenomena* to be observed in passing from the colloids either in the direction of the coarse dispersions or in that of the molecular systems? Following our definition of colloids we are not only justified but in duty bound to ask this question. I have already showed you how the colors of such colloid metals as gold change from red to violet and blue as the degree of dispersion decreases. But what is the color of less colloid or coarsely dispersed gold? Thin leaves of gold have in transmitted light a distinctly greenish color, and I have told you that gold may be obtained as a greenish precipitate. But what is the nature of the transition phenomena as we pass from the colloid to the molecularly dispersed or ionically dis-

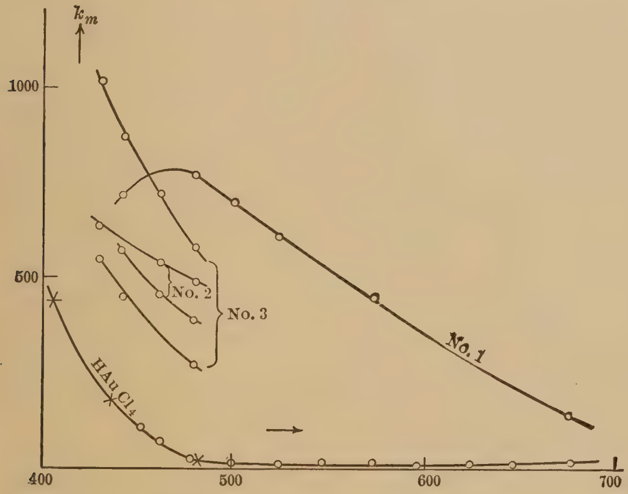

FIG. 25.—Variation in light absorption by colloid gold with change in its degree of dispersion according to The Svedberg. The curve farthest to the right is that of the coarsest colloid. The curve farthest to the left is that of a molecularly dispersed gold colloid solution.

persed gold? The most highly dispersed colloid gold thus far prepared is ruby-red or yellowish-red.[1] Ionic gold in the presence of a colorless anion is distinctly brownish-yellow or orange. An accurate study of this transition cannot be made with the naked eye, but may be made spectroscopically. In this way THE SVEDBERG has shown that the absorption curves of colloid gold gradually *approximate the absorption curves of ionic gold as the degree of colloid dispersion increases.*[2] The curves of Fig. 25 illustrate this. The lowermost curve is the absorption curve of molecular gold chlorid. The uppermost one is that of a relatively coarse colloid gold. The curves between are those of colloids of successively greater degrees of dispersion.

Let us consider next the colors of colloid silver. Here also the color passes from yellow through orange, red, violet and blue to green in the coarsest members of the series. But according to G. QUINCKE and others, the color of thin silver foil is also blue or green. The transition from the colloid realm to that of the coarse dispersions is therefore perfectly smooth. On the other hand, the most highly dispersed silver colloids are a transparent yellow or greenish yellow; in other words, they absorb chiefly violet and ultraviolet light. The more highly dispersed, the greater is the transparency of these silver colloids. When prepared from very dilute solutions, or, differently expressed, under conditions which yield colloids of particularly high degrees of dispersion, the yellow of these colloids becomes so faint as to be hardly recognizable. But this gradual disappearance of color in a highly dispersed colloid silver marks the passage from the color of the colloid into that of the silver ion. The latter, in the presence of a colorless anion, is colorless.

Similar considerations hold for the colors of colloid platinum. The most highly dispersed colloid platinum known,

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[1] See THE SVEDBERG, Koll.-Zeitschr., **4**, 168 (1909); **5**, 318 (1909).

[2] See THE SVEDBERG, l.c., as well as numerous other papers appearing in the Kolloid-Zeitschrift and the Zeitschrift für physikalische Chemie.

that prepared by L. Wöhler, is orange red, while the color of platinum salts is orange yellow.

What has been said above holds not only for the colors of colloid metals but for those of the organic colloid dyes as well. I show you in Fig. 26 the absorption curves of indigo of different degrees of dispersion (The Svedberg). In colloid form in aqueous solution indigo is blue, but, when molecularly dissolved, as in hot petroleum or chloroform, it is red to violet. The lowermost curve (2) shows the absorption spectrum of an old and therefore relatively coarsely dispersed colloid; curve 1*A*, the absorption curve of an ordinary colloid; curve *B*, that of a molecular indigo in chloroform. You observe how the curves lie progressively higher as the degree of dispersion increases, while at the same time they move from the side of the shorter wave lengths to that of the longer.[1]

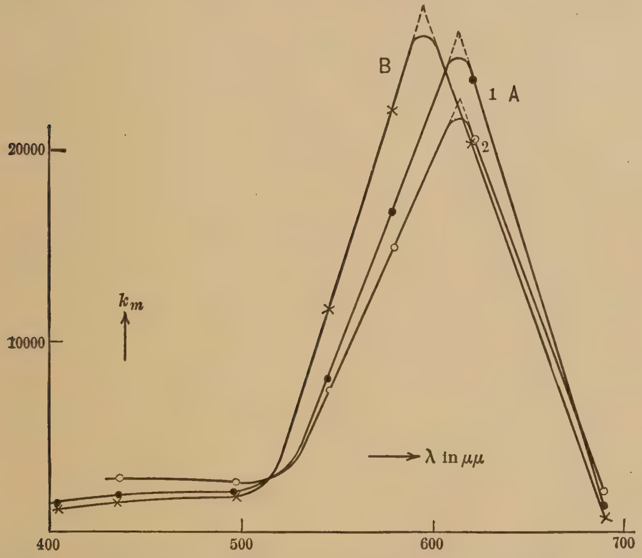

Fig. 26.—Absorption of light by indigo solutions of different degrees of dispersion.

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[1] In the experiments represented in the figure, the concentration of the colloids is only about half that of the molecular solution. The specific color intensity may not therefore be deduced from the figure. See The Svedberg, Die Existenz der Moleküle, 51.

§14.

The principle of continuity holds not only for the intensity and quality of the colors of dispersed systems but also for their *optical rotation.* Fig. 27 shows a series of curves which E. NAVASSART and I[1] obtained in a study of the optical rotation of tannin of different degrees of dispersion. The ordinary aqueous solution of tannin, made by dissolving tannin in water, represents a *polydispersoid,* in other words, one in which there are particles of different degrees of dispersion. Most of the tannin is in colloid solution yet some of it, as even GRAHAM knew, will pass through parchment paper, and is therefore in a state of higher dispersion. By using different grades of dialyzing membranes we can obtain different fractions of the aqueous tannin. Tannin is molecularly soluble in organic solvents. When the optical rotations of these different tannin solutions are compared, the coarsest tannin is found to produce the greatest rotation, the molecularly dispersed tannin the

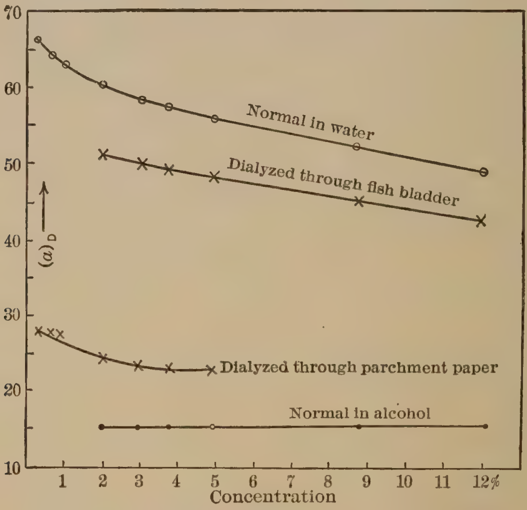

FIG. 27.—Influence of degree of dispersion upon the optical rotation of tannin.

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[1] E. NAVASSART, Koll.-Zeitschr., **12**, 97 (1913); Kolloidchem. Beih., **5**, 299 (1914).

least. The behavior of two such tannin solutions, representing the extremes of dispersion, is indicated in the uppermost and lowermost curves of Fig. 27. Between them are found the curves characteristic of tannin solutions which have dialyzed through parchment paper and fish bladder. These membranes have different sized pores, the fish bladder allowing larger aggregates to pass through than the parchment paper. As the order of the curves shows clearly, the specific optical rotation increases progressively in passing from the molecularly dispersed tannin to its colloid form.

I believe you will agree with me when I say that a study of the changes in optical properties accompanying changes in the degree of dispersion proves in unequivocal fashion the correctness of the principle of continuity.

§15.

Not all the physical properties of dispersed systems have as yet been studied systematically from this point of view. But this is hardly to be wondered at, for this way of looking at the question is not yet ten years old.[1] We strike a difficult and still ill-defined field in the general relations between degree of dispersion and the *electrical* behavior of colloids. Since it covers a series of properties which play a great rôle in special colloid chemistry I shall touch upon it briefly.

Most colloid systems, like most coarse dispersions, have an electric charge. We recognize it and its sense by sending an electric current through the system. When electrically charged, a colloid moves in an electric field — we observe the phenomenon of electrophoresis. The migra-

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[1] Wolfgang Ostwald, Koll.-Zeitschr., **1**, 291, 331 (1907); also Grundriss der Kolloidchemie, 1. Aufl. Dresden, 1909. Here was emphasized, so far as I know for the first time, the importance of the study of these transition phenomena and here too was suggested the curve-like nature of the variations in physico-chemical properties with changes in degree of dispersion. Two years later appeared the observations of The Svedberg and his pupils which followed the suggestions of my earlier papers.

tion of a colloid is easily seen when the points of two wire electrodes are dipped into a drop of any dispersoid on a microscopic slide, or when the dispersoid is poured into a U tube and a current is sent through it. I show you here two U tubes in one of which I have a mastic sol, in the other a colloid iron hydroxid (demonstration).[1] The electric current of the laboratory (110 volts) has been passing for about five minutes through both.[2] The tubes have been placed in parallel. To the right is the positive pole, the anode. You observe how in the tube containing mastic the liquid is almost colorless about the cathode, while a thick white mass has collected about the anode. Colloid mastic wanders to the positive pole. It is therefore negatively charged. A reverse behavior is observed in the iron hydroxid. The colloid has collected in thick flakes about the cathode. It is therefore positively charged.

It is often possible to detect the sense of the electric charge of a colloid, even without the aid of a current, by very simple means. I have hung up here some strips of ordinary filter paper, the lower ends of which may be dipped into different colloid solutions. As you know, liquids tend to ascend such strips of filter paper through capillarity. I have here the colloid solutions of two blue dyes, alkali blue and night blue. Let me dip the ends of two filter paper strips into them, and even as I talk to you, you note the following: in the alkali blue the dye ascends together with the aqueous dispersion medium. The water is slightly ahead, but nevertheless the dye follows close behind. In fifteen minutes it may have covered ten or more centimeters (demonstration). The night blue behaves totally differently. The water ascends far in advance of the dye. In other words, there is a separation of the dye

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[1] Instead of these colloids, berlin blue or colloid graphite (negative) or night blue and alkali blue (positive and negative) may be used.

[2] Since the speed of electrophoresis is roughly proportional to the difference in potential, it is well to use currents of high potential and small amount. Overheating and the disturbances incident thereto must be carefully avoided.

from the dispersion medium. After a quarter of an hour the dye will have concentrated at a point a little above the surface of the liquid, but it will not have followed the water (demonstration).[1]

Let me next show you two experiments with different colloids of graphite (demonstration). The dispersed phase, the graphite, is the same in both, but the dispersion media are different. The two have been subjected to a "capillary analysis." This first dish contains colloid graphite in water (aquadag); the second, colloid graphite in mineral oil (oildag) diluted somewhat with ligroin. The watery colloid has ascended with the water, but in the oily colloid the colloid phase has concentrated below, while the dispersion medium has alone ascended the strip.

According to F. Fichter and N. Sahlbom this difference in ascent is to be explained through *the difference in the electric charge* of the colloids. *Negatively* charged colloids ascend with their dispersion media, while the *positively* charged are held fast near the surface of the liquid and therefore separate from their dispersion media. The explanation of this is to be found in the fact that filter paper in contact with water assumes a negative electrical charge. Therefore when a positively charged colloid comes in contact with the paper the colloid becomes fixed electrostatically. A negatively charged colloid, on the other hand, because of the similarity of the charges, goes by undisturbed.[2]

An important and much overlooked fact regarding this electric charge of one and the same dispersed phase is its

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[1] Particularly suitable concentrations are 0.2% night blue and 1.0% alkali blue.

[2] The experiment with colloid graphite in ligroin is not free from objections. It is possible that the filter paper assumes toward ligroin and like substances a different charge than toward water. To explain the behavior under such circumstances, the second assumption would have to be made that the graphite in oil maintains its negative charge, which according to the experiments of G. Quincke is not true for the charge of sulphur particles in turpentine and in water [Wiedemann's Annalen, **113,** 513 (1861)]. A careful study of these relationships as well as of the whole capillary method

variability.[1] *As a rule,* colloid metals and sulphids, for instance, show a negative electrical charge, especially in aqueous dispersion media. Colloid iron hydroxid is usually positively charged; we are, however, familiar with negatively charged iron hydroxid sols. A striking illustration of the variability of the electric charge in one and the same colloid is furnished by the following experiment of A. LOTTERMOSER. Either a positively or a negatively charged silver iodid may be obtained at desire by mixing a dilute solution of silver nitrate with one of potassium iodid. When the potassium iodid is poured into an excess of silver nitrate, we obtain a positively charged colloid. If we proceed in a reverse way, pouring the nitrate into the iodid so that the latter is present in excess, we produce a negatively charged colloid.

Then there are colloids which have only a very faint electrical charge. Protein and starch solutions very free of electrolytes belong in this class. Through the addition of aluminium sulphate, colloid gold can also be "discharged," or "oppositely" charged, so that it either may not move at all in an electric field or may move toward the negative pole.

The *velocity* of colloid migration practically equals that of ions and coarsely dispersed particles. But since accurate studies are still lacking on this relation of degree of dispersion to speed of migration in an electric field, it may not yet be concluded that the latter is independent of the former.[2] Even among the molecular dispersoids the larger and more complex ions migrate more slowly than those

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of FICHTER-SAHLBOM is much needed since the experimental facts do not always agree with the simple scheme outlined in the text above. See A. W. THOMAS and J. D. GARRAND, Chem. Zentr., 1114 (1918); WOLFGANG OSTWALD, Kolloidchem. Beih., **10,** 197 (1909); R. KELLER, various papers in the Kolloid-Zeitschrift since 1920, etc.

[1] Insufficient consideration is given the fact that not only the amount but the *sense* of the electric charges in dispersed systems vary as greatly as the degree of dispersion. See WOLFGANG OSTWALD, Koll.-Zeitschr., **22,** 79 (1918).

[2] See for example H. FREUNDLICH, Kapillarchemie, 233, Leipzig, 1909 but also the newer views of G. VON HEVESY, Koll.-Zeitschr., **21,** 129 (1917).

of higher dispersion. It is reasonable to expect, therefore, that colloids will move still more slowly.

When we inquire about transition phenomena, the dearth of available systematic investigations and the complexity of the phenomena make it impossible to establish here as simple and definite relations as were possible when discussing optical properties. Even the newer literature still argues the question of whether colloids are "ions" or not. In answering this, much depends on what we understand by "ions." If the term is used simply to cover all material carriers of electricity, then colloids and even coarsely dispersed particles must be regarded as ions, for masses of electricity are, of course, transported whenever any of these dispersed particles move in an electric field. But if by ions we mean only those material carriers of electricity which follow the laws of FARADAY, as do the ions in salt solutions, if, in other words, the particles must always be the carriers of equivalent amounts of electricity, then colloid and coarsely dispersed particles are not to be counted among them; for to the present time no one has proved the validity of FARADAY's law for electrophoresis; and present knowledge indicates that the law does not hold in its ordinary form for colloids.[1] The influence of concentration upon electrophoric "conductivity" seems to be quite different in the case of the colloids and coarsely dispersed systems from that of a similar change in the case of the molecularly dispersed electrolytes. There exist, however, some interesting analogies between the behavior of colloids and the properties of gaseous ions, in other words, those responsible for electrical conductivity in gases.[2] Among these, too, are such as do not follow FARADAY's law. Here the influence of changes in

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[1] For further details regarding discrepancies between the behavior of normal and of colloid ions, see, for example, WOLFGANG OSTWALD, Koll.-Zeitschr., **7**, 132 (1910). The mathematics on page 152 of this article regarding the similarities in the diffusion coefficients is, however, incorrect, since in the definition of diffusion coefficients an error was made in their values.

[2] See the preceding footnote.

concentration upon the conductivity of the gas is not the same as that observed in aqueous electrolytes. Just as in the case of colloid electrophoresis, we know gaseous systems in which predominate carriers of one kind, either positive or negative ions. In them electricity is carried predominantly in one direction. The migration of gaseous ions under the influence of an electric current may be deviated by exposure to a magnetic field. This is a phenomenon which may be observed in colloids,[1] but not in normal aqueous electrolytes. These considerations would seem to indicate that further investigation of the analogies between electrophoric phenomena as observed in colloids and gases is likely to yield simpler and better material for the establishment of our principle of continuity than has thus far the study of the analogies between colloids and aqueous electrolytes.

§16.

Allow me in conclusion to touch upon a series of properties which again show the importance of the degree of dispersion upon the physico-chemical behavior of dispersed systems. It is a fact which has as yet received too little attention that such fundamental values as the maximum *solubility*, the *freezing point* and the *melting point* of a substance vary in marked fashion with the size of the particles of the material concerned. Thus, as far as known, the solubility of solids (in molecularly dispersed form) always *increases with increase in the degree of dispersion.* The old experiments of G. Stas already suffice to show how true this is. Stas found the solubility of silver chlorid in the precipitated form (in other words, as particles of approximately colloid size) to be a hundred times greater than the solubility of this same substance when granular or coarsely dispersed.[2] This behavior

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[1] See J. J. Kossonogow, Koll.-Zeitschr., **7,** 129 (1910), as well as my remarks following Kossonogow's paper.

[2] For details and for further examples see Wolfgang Ostwald, Handbook of Colloid Chemistry, trans. by Martin H. Fischer, second English edition, Philadelphia, 1919. See also the newer work of T. Glovezynski, Kolloidchem. Beih., **6,** 147 (1914) who could confirm the findings of Stas only in part.

is not peculiar to silver chlorid, but holds for all solid substances. In analogous manner, the freezing point of water is lowered, not only through the presence in it of molecularly dispersed phases but simply by being allowed to freeze in a *dispersed* form, as when it is confined in capillary spaces. The water which has been allowed to soak into a clay sphere does not freeze until – 0.7° C., and wet filter paper does not stiffen until – 0.1° C. is reached. These are not simply phenomena of mere under-cooling, let it be noted. Looked at from the ordinary point of view, these facts simply indicate that determinations of the freezing point, were they carried out in capillary tubes, would always show too great values. But regarded from the point of view of the dispersoid chemist, they cannot help but suggest that the lowering of the freezing point in molecularly dispersed systems is also nothing but a "capillary" phenomenon; to him, the presence of molecules and ions divides the solvent into many tiny capillary divisions through which the slight depression of freezing point noted, for instance, in the coarsely dispersed clay sphere, is compounded to attain the great values characteristic of molecularly dispersed solutions.[1]

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[1] One might assume that the depression of the freezing point of a dispersoid is proportional to its internal specific surface, in other words to the quotient of surface of the dispersed phase (per unit weight) and the volume of the dispersion medium. The value Δ mol. = 1.84°, the molar depression of the freezing point of molecularly dispersed aqueous systems, would then represent the capillary depression of maximally dispersed systems (molecules and ions) containing one mol of the dispersed phase in the liter of water. In such maximally dispersed systems matters may then be simplified by substituting for the specific surface the concentration of the dispersed phase, that is to say, the number of particles in the unit volume, since in such maximally dispersed systems all the particles have practically the same size. Such conditions obtain, however, only in extreme cases as in "infinitely" dilute solutions and not in concentrated solutions nor in such as are admixed with polymeric, associated or colloid particles. All the latter yield too small depressions of the freezing point as compared with the molecular solutions. In order to get the normal, maximal Δ value in such instances, a larger number of the large particles must be present in the unit volume.

If, for simplicity's sake, we assume a simple proportion to exist between specific surface and freezing point depression, the specific surface (Ωm) of

The melting point of a substance also changes with the degree of its dispersion. It is lower as the degree of dispersion is increased. Few of the organic chemists, who make

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molecular particles of an average diameter of 0.1 $\mu\mu$ to the specific surface (Ωk) of colloid particles having a diameter of 100 $\mu\mu$, if both were spheres, would be as about $5.10^8 : 5.10^5$ or as 1000 : 1. See WOLFGANG OSTWALD, Handbook of Colloid Chemistry, translated by MARTIN H. FISCHER, second English edition, 91, Philadelphia, 1919. In order to obtain the same specific surface, 1000 times as many colloid particles would therefore be needed in the same unit volume as when molecules are used.

In order to obtain the normal or maximal depression of the freezing point in water, a gram-molecule (197.2 grams) of gold, or, roughly, about 200 grams, would therefore have to be molecularly dissolved in 1000 cc. of water. A molar solution of molecularly dispersed gold would therefore contain about 20 percent gold; a molar colloid solution of gold possessed of the same specific surface would have to contain $\frac{200 \times 1000}{1000}$, in other words, 200 parts of gold to one part of water. This means that not until we dealt with a gold mud containing 99.5 percent colloid gold and about 0.5 percent water would we obtain a depression of the freezing point of 1.84°. A gold mud made up of particles 100 $\mu\mu$ in diameter and containing about 5 percent of water would show a Δ value of about 0.1°. The same value would be shown by a mud containing particles 10 $\mu\mu$ in diameter and about 33 percent of water. On the other hand, a 2 percent gold sol (which belongs to the most concentrated of the gold sols that can be produced under normal circumstances) would, if its particles were 100 $\mu\mu$ in diameter, be expected to show a depression of only 0.00018°; if the particles were 10 $\mu\mu$, a depression of 0.00184. These are values which correspond with those obtained experimentally.

If we assume further that the capillary depression of the freezing point is independent of the specific chemical composition of the dispersed phase as taught in the classical solution theory, a dispersoid like wet filter paper which shows a Δ value of $-0.1°$ and is possessed according to H. BECHHOLD of pores about 1 $\mu = 1000\ \mu\mu$ in diameter, would have a concentration of 99 per cent solid material or a water content of about 1 percent. Similarly, a dispersoid of the type of the clay sphere of VON BACHMETJEW, to which a pore value not exceeding 200 $\mu\mu$ may be attributed, and which shows a Δ of $-0.7°$ would have a concentration of 99.3 percent or a water content of about 0.7 percent. As a matter of fact, much larger amounts of water have probably been absorbed in both these instances, even though the depression of the freezing point would theoretically be expected to be greatest when the water content is lowest. The facts argue for the conclusion that at least a part of the pores and spaces in filter paper and clay spheres are decidedly smaller than the assigned values. This conclusion is in harmony with the observed facts. The presence, moreover, of molecularly dissolved impurities also tends, naturally, to give the observed depressions of the freezing point fictitiously high values.

These remarks are merely intended to indicate the possibilities of a capilsuch melting point determinations almost daily, know how great such lowering may be. P. Pawlow,[1] for example, found finely powdered salol, antipyrin, etc. (but in which the individual particles were still microscopically visible) to melt at a temperature 7° below that at which larger particles did. F. Meissner,[2] on the other hand, states that this effect does not appear until the particles are submicroscopic in size, so that the question of just where such an effect becomes appreciable is still debatable.

Imagine such changes as observed in these relatively coarsely dispersed systems to be continued over into the realm of the colloids. It seems as if *every* property may in this realm assume a new value, wherefore we need not be surprised to find colloids exhibiting physico-chemical reactions which the coarsely dispersed material shows not at all.

According to what is known as Wenzel's law, the *reaction velocity* of solids with liquids is proportional to the area of contact. It need not surprise us to find, in consequence, when the enormous surface presented by a colloid becomes available for reaction purposes — we shall return to this point in a later lecture — that colloid sulphur, for instance, acts as an energetic reducing agent for silver salts, a property which coarsely dispersed sulphur does not show at all;[3] and that colloid platinum still decomposes hydrogen peroxid when but one gram atom of the metal is present in seventy million liters of the dispersion medium (G. Bredig). We shall have occasion later to return to these catalytic effects.

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lary theory of these and allied phenomena. For the detailed development of such, quantitative experiments must first be carried out in coarsely dispersed systems like capillaries. That measurements upon such coarsely dispersed systems may be used after the fashion of the well known experiments of J. Perrin for the calculation of the constants of molecularly dispersed systems can also merely be pointed out here.

[1] P. Pawlow, Koll.-Zeitschr., **7**, 37 (1909) where references to his earlier work may be found.

[2] F. Meissner, Zeitschr. f. anorg. Chem., **110**, 169 (1920).

[3] M. Raffo and A. Pieroni, Koll.-Zeitschr., **7**, 158 (1910).

We need not, however, be surprised to find that still more highly dispersed metallic colloids prove *less* effective in decomposing hydrogen peroxid,[1] for we know that molecularly or ionically dispersed platinum (such as platinic chlorid) has but slight or no catalytic action. We observe again a curve showing a maximum and one of the same type, therefore, as previously noted in discussing the relation between color intensity and degree of dispersion. Coarsely dispersed and molecularly dispersed metals have little or no catalytic action, while those colloidally divided work most energetically. At a certain point in this middle region appears the maximum.

§17.

The subject of the relation between physico-chemical properties and degree of dispersion is very great and I could continue much longer with it, but perhaps I have tired you already. If so, I beg you to remember that the whole present day concept of the colloids stands and falls with the recognition of these relations. We are justified in regarding the colloids as special examples of the dispersed systems only if we are able to show that the properties of colloid systems blend gradually into the properties of the coarsely dispersed systems on the one hand, and into those of the molecularly dispersed on the other. This new concept is but a flimsy hypothesis as long as it cannot be experimentally proved.

I hope that I have succeeded in bringing you such *experimental* proofs, even though, as I have emphasized, many parts of the subject have not yet been worked out in detail. *The primary characteristic of a colloid is its special degree of dispersion.* If this is true, then *colloid chemistry becomes primarily not the science of the properties of a special group of substances, but that of the properties of a physico-chemical*

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[1] See St. Rusznyak, Zeitschr. f. physik. Chem., **85**, 681 (1913).

state into which any substance may be brought.[1] Like the science of crystallography, colloid chemistry deals with a special physico-chemical state of matter. There exists, of course, a *special* colloid chemistry also which details the specific variations which any chemical substance may show when it happens to appear in the colloid state, just as remarks attached to a discussion of any chemical substance which are crystallographic in character may be found in our text-books. Formerly it was believed that colloid chemistry had spent itself when it had thus described in footnote fashion the colloid properties of chemical compounds. Today we insist upon the existence of colloid chemistry as an *independent* division of the physico-chemical sciences. It is the *science* of the colloidally dispersed state. The establishment of this fact was, in brief, the main purpose of today's lecture.

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[1] Since in recent years this conclusion has often been attributed to P. P. von Weimarn I may be permitted to point out that it is mine; see Oppenheimer's Handbuch der Biochemie, **1**, 853 (1908); also Grundriss der Kolloidchemie, 1. Aufl., Dresden, 1909.

III.

THE CHANGES IN STATE OF COLLOIDS.

THIRD LECTURE.

THE CHANGES IN STATE OF COLLOIDS.

Our previous lectures have dealt for the most part with the general physical chemistry of the *colloid state,* or of the *dispersed state in general.* I have tried to show you where the colloid systems fit into the great general scheme of the dispersed systems. Today we shall discuss the colloidally dispersed systems more specifically. This does not mean, of course, that these possess properties for which there are no analogies in the neighboring realms of dispersion, for, as already emphasized, we pass gradually from the coarse dispersions into the colloids and through these into the molecularly dispersed systems — but a whole series of phenomena shows itself either most markedly or least intensely in the colloid realm and may in this sense be regarded as specific for the colloid state. These phenomena will absorb our chief interest today, and it will be our special problem to discover what special changes these typical colloids suffer when exposed to different external conditions. We shall, therefore, start with colloid systems, expose them to different experimental conditions and see what happens. What we observe may justly be termed the *special* physical chemistry of the colloid state.

§1.

The considerations of our previous lectures again permit us to predict what must be the nature of a large number of these changes in the colloid state. Ignoring certain radical changes which have to do with gross destruction of the colloid itself by chemical means, what are the changes which a colloid may suffer? It may, first of all, undergo changes in its degree of dispersion. These changes may be limited to the region of the colloid realm itself, or they may extend beyond this into the realms of the molecularly dispersed or the coarsely dispersed. These changes which occur within the limits of the colloid realm itself we call the *internal* changes in state, thus distinguishing them from the *radical* changes in state which take us beyond these limits. Of particular importance are the changes in degree of dispersion occurring at the limit between coarsely dispersed and colloid systems. *Decreases* in degree of dispersion resulting in coarsely dispersed systems are designated *coagulations.* Liquid colloids are also known as *sols;* their coagulation products, as *gels.* *Increases* in degree of dispersion are designated *peptizations,* because they simulate the solution phenomena observed when solid proteins are acted upon by ferments. Obviously these two great classes of changes in state can be foretold.

§2.

Another great group of changes in state is connected with changes in the *type* of the dispersed phase in colloids. You will recall that there are colloids of the composition solid + liquid (suspensoids) and liquid + liquid (emulsoids). We shall consider these in detail today. It is an interesting fact that one and the same colloidally dispersed material may vary in one and the same dispersion medium between solid and liquid; as we shall see later, the colloid particles may pass *gradually* from the solid to the liquid state. This is particularly true of the hydrated or solvated colloids, in which the dispersed particles carry about with them more or less of the dispersion medium in combined form. The process is analogous to the behavior of a piece of gum arabic which may show all transitions from a brittle solid to a liquid, depending upon the amount of water it has taken up. After I have showed you the experiments accompanying today's lecture, you will be astonished at the great rôle played by these changes in the type of the dispersed particles. The phenomena of gelation and of swelling belong under this heading.

§3.

But we can foresee the existence of even a third class of changes. Were you ordered to sketch a colloid you would no doubt make it look something like Fig. 28, *A*. You would naturally assume that the colloid is distributed uniformly through the mass. But closer study shows that this is only approximately true. Wherever the colloid comes in contact with a surface (as the vessel wall or the air) it fails to maintain a uniform spacial distribution. At the surfaces of contact the concentration becomes different from that obtaining in the inner parts of the colloid mass. The surfaces contain either less or more of the dispersed phase than the rest of the system, as indicated in Fig. 28, *B*. Usually the colloid tends to concentrate in the surfaces. These changes in concentration are commonly designated as *adsorption*. It was the American giant, WILLARD GIBBS, who first pointed out that at the surfaces of dispersed systems a different concentration was to be expected than prevails in the body of the dispersoid. GIBBS did not, of course, either know or use this modern concept of the dispersed systems, but his deductions were of such general nature that they apply also to the special field which we are discussing. Adsorption phenomena are of great variety and play a great rôle in many different ways in the changes in state of colloids.

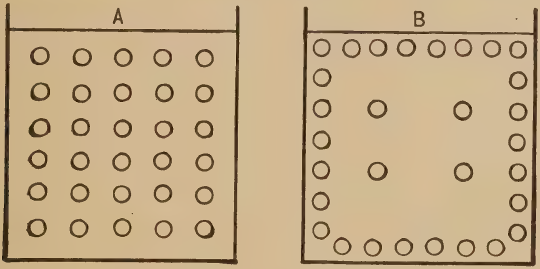

FIG. 28.—Diagram illustrating the concept of adsorption.

It must be remembered that changes in degree of dispersion, in type of dispersed phase and in its spacial distribution, constitute by no means all the possible changes in state. Neither do these three groups of phenomena appear singly; they frequently appear in combination. The many combinations possible and the innumerable resultant changes in state constitute the prime reasons for the great instability of the colloids. Even GRAHAM said that rest never ruled in the colloid state. These facts render apparent why the scientific study of the changes in state of colloids is of such great interest and why such particularly complicated phenomena as those of life take place in colloid media and only in such.

§4.

But let us leave these theoretical considerations and return to the experimental. By what experimental methods may we study qualitatively and quantitatively the changes in the state of colloids? A first fact ever to be borne in mind is that changes in the state of a colloid always take time; differently expressed, they occur at definite velocities. They take time as do chemical reactions, but differ from these in that their end states are not so clearly defined. The end products of a chemical reaction are definite chemical compounds with constant properties; the changes in state of a colloid may halt when any degree of dispersion or hydration has been attained. The kinetic element, therefore, serves to characterize colloid changes in state even more markedly than it does the changes observed in the fields of "pure" chemistry. It is for this reason that the ideal method of studying colloid changes always proves to be a *kinetic* one. But it also follows that the characteristics of gelation, of swelling, of coagulation, etc., will never be marked by clearly defined "points." For instance, it is impossible to say that a protein solution coagulates when the concentration of twenty percent ammonium sulphate has been reached. A "slight turbidness" is likely to be observable at ten percent; a "marked turbidness," at fifteen percent; a "beginning precipitation," at seventeen percent, etc. Nor will such a protein be suddenly coagulated if its temperature is decreased a degree. The expression of such findings in the terms of kinetics is far better.[1]

In the case of the simpler changes in the colloid state, as when the degree of dispersion is merely altered, we may follow the changes in the size of the particles by employing the ultramicroscope, ultrafiltration, etc., and plotting the results as a velocity curve; or we may utilize the principle discussed in a previous lecture according to which every physico-chemical property of a colloid varies with its degree of dispersion. In this way I demonstrated to you the increase in the size of the particles during coagulation in a gold sol when calling your attention to the changes in color from red to blue. In complicated cases we still have recourse to such *indirect* methods. We measure, for example, changes in conductivity, in turbidity, in viscosity, etc., and then from their value parallel them with changes in the state of the colloid. Of course, we try to choose properties which are easily measured and of such prominence as to change with but slight alterations in state. The methods must, moreover, permit a study of the changes in state without causing a destruction of the colloid itself.

We observe changes in the internal state of colloids in great variety in such materials as gelatin, albumin, rubber or cellulose. We have called these colloids solvated emulsoids and will learn more of them shortly. One of their most conspicuous physico-chemical properties and one intimately associated with their internal state is their *viscosity*. No better example of its importance can be given than appears in the fact that the FARADAY SOCIETY in 1913 devoted a

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[1] So far as I know, I was the first to emphasize that changes in state should by definition receive kinetic treatment instead of being characterized by the customary "points." See my Grundriss der Kolloidchemie, 1. Aufl., 267, Dresden, 1909; also, Koll.-Zeitschr., **12**, 218 and 246 (1913); Die neuere Entwicklung der Kolloidchemie, 18, Dresden, 1912. Following these suggestions of mine, there appeared the papers of H. PAINE, H. FREUNDLICH, N. ISHIZAKA, etc. See Koll.-Zeitschr., **11**, 115 (1912); Koll.-Zeitschr., **12**, 230 (1913); Kolloidchem. Beihefte, **4**, 24 (1912), where references to further papers will be found.

whole meeting to its discussion.[1] Over a dozen colloid chemists spent two sessions on this special theme. Nor could I do better to illustrate the variety and importance of the internal changes in state of which a colloid is capable than by giving you an outline of some viscosity studies.

§5.

Anyone who has busied himself with dialysis or diffusion experiments soon discovers that there are two distinct classes of colloids among the many non-dialyzing, non-diffusing dispersoids with which he may work. Their behavior is totally different. Especially evident is the great viscosity of the one as compared with that of the other. Colloids of gold or of the metallic sulphids hardly alter the viscosity of their dispersion media. In low concentration these colloids are as mobile as their "solvents" by themselves and even in high concentrations their viscosity increases are only arithmetic in type. This is shown in curve *A* of Fig. 29. The behavior is characteristic of the solid + liquid type of colloids, the suspensoids.

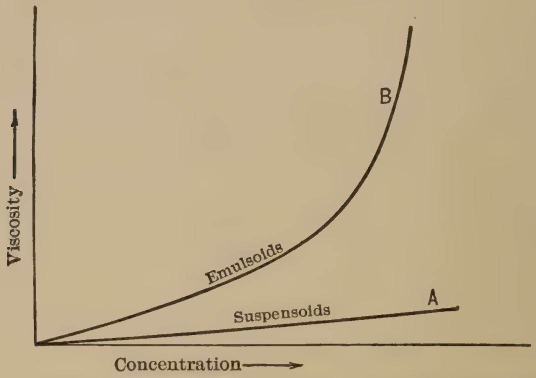

Fig. 29. — Diagram illustrating the relation between viscosity and concentration in different types of colloids.

Colloids like gelatin which we said above are hydrated emulsoids behave entirely differently. They show enor-

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[1] See Koll.-Zeitschr., 12, Heft 5 (1913).

mous viscosity values in even very low concentrations, and with every increase in the concentration of the colloid, the viscosity value mounts enormously, as shown in curve *B* of Fig. 29. As you know, gelatin in water shows all possible viscosity values from that of pure water to that of a solid jelly within the concentration realm of a two percent solution. We know other emulsoids which will show such variations from unit viscosity to infinity (the viscosity of solids) within even narrower ranges of concentration. Castor oil soap, for example, is an almost solid jelly at a concentration of 0.1 percent, if a certain amount of alkali is present; and similarly striking figures may be cited for other organic colloids.[1]

§6.

Besides these great absolute and relative effects of concentration upon viscosity, other factors influence it, as *temperature*. As you know, the viscosity of molecules decreases steadily with increase in temperature. The viscosity of pure water, for instance, decreases some 2 percent for every degree of rise in temperature between 0° and 25° C. But in gelatin solutions such decrease in viscosity is enormously greater. In concentrated solutions or in gels the decrease is so great within certain temperature limits that phenomena are observed which seem analogous to the melting of homogeneous solids. Within a temperature range of but a few degrees, there occurs a fall in viscosity from the values characteristic of solids to those characteristic of fluids. It is an important fact, too, that the observed change is a progressive one and not such a sudden change in state as is observed, for example, in the melting of a crystal.

High viscosity values are observed even in *non-solvated emulsoids*. Concentrated sulphur solutions, for example, may show a salve-like consistency. There exist many

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[1] Further examples are detailed in the paper of W. Döhle, Koll.-Zeitschr., **12,** 73 (1913).

theoretical reasons why the liquid state of the dispersed phase should alone suffice to explain on a physical basis the great viscosity of the emulsoids.[1]

§7.

Besides concentration and temperature, other less drastic changes in external conditions alter the viscosity of solvated emulsoids. Simple shaking or repeated passage through a capillary, for instance, often suffice to decrease viscosity as has been observed in milk. The viscosity also falls when emulsoids are kept for a time at higher temperatures. In fact, time alone will effect viscosity changes. A colloid needs but to be left alone for a time in order that changes in its viscosity may be observed, — sometimes an increase, as in gelatin, at other times, a decrease, as in starch.

Of course, the addition of extraneous substances, both electrolytes and non-electrolytes, suffices to influence the viscosity of colloids. I show you here a series of gelatin solutions to which various substances have been added (demonstration). The first tube contains a pure two and one-half percent gelatin. It is, as you see, a solid jelly which on hard shaking separates in pieces from the wall of the tube. The second tube contains the same concentration of gelatin, but to it have been added several percent of dry magnesium sulphate. The jelly is decidedly stiffer and does not break to pieces on hard shaking. The sulphates, citrates, phosphates, etc., all increase the viscosity of aqueous colloids of the type of gelatin, and of course, to a much greater degree than when added to pure water. The third tube again contains the same gelatin but this time some potassium iodid crystals were added to it. As you observe when I tilt the tube, the gelatin has remained fluid. Iodids, bromids, cyanids and certain chlorids decrease the viscosity when present in certain

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[1] See especially E. Hatschek, Koll.-Zeitschr., **7,** 81, 301 (1910); **8, 34** (1911); **11,** 280, 284 (1912); **12,** 283 (1913); **13,** 88 (1913).

concentrations. The remaining tubes show the effects of some added non-electrolytes. Chloral hydrate and urea decrease viscosity. Alcohol in small amounts increases it. This problem of the effect of added substances becomes much complicated by the fact that one and the same substance may either increase or decrease the viscosity, *depending upon the concentration in which it is added.* Thus, gelatin solutions to which acid or alkali is added in different concentrations show a minimum and a maximum of viscosity, while when chlorids are added several minima and maxima of viscosity may be noted.

All these variations in viscosity correspond to changes in the state of the colloid systems themselves, such as changes in degree of dispersion, in type of dispersed phase or in degree of solvation. We know, for example, from ultramicroscopic and other means of investigation that in the ageing of dilute starch there occurs not only a decrease in dispersion but also a dehydration of the dispersed phase. The colloid particles not only give off a part of their water but they clump to form larger aggregates. Here a decrease in the viscosity parallels a decrease in dispersion and a passage from the liquid state toward the solid. Conversely, the addition of alkali or acid in certain concentrations may increase the hydration of certain colloids, as those of protein. Here the dispersed phase moves from the solid toward the liquid side, a change which again betrays itself by an increase in viscosity.

With other colloids we are not yet sure what special internal changes in state are responsible for the extreme variations in viscosity. According to recent studies it seems probable, for example, that gelatin solutions while cooling develop an internal structure; in other words, the coalescence of the colloid particles yields aggregates that form fibrils, nets, etc. We shall return to this question later. The effect of adding certain substances, as salts in different concentrations, cannot as yet be connected in any satisfactory way with the accompanying changes in degree of dispersion and of hydration. To get light here we need to supplement the general methods of physico-chemical investigation with the colloid-chemical ones of ultramicroscopy, ultrafiltration, etc.

§8.

Our discussion of gelation brings us into the field of the changes in state which occur within the limits defining the realm of the colloids themselves. Let us begin by asking what happens when a gelatin solution cools and sets. What are the internal changes which lead to the enormous increases in viscosity that are observed, for instance, when the originally liquid mass gradually changes into a solid? Let me illustrate the theory of gelation by an experiment.

I have in this flask two liquids which at ordinary temperature are only partially soluble in each other, namely, phenol containing some water, and water containing a little phenol. Even at a distance you observe that they scarcely dissolve in each other, for as soon as I shake the flask the mass of liquid shows the white color of an emulsion (demonstration). The solubility of phenol and water in each other increases greatly with increase in temperature. To prove this I heat the mixture while continuously shaking it (demonstration). As soon as I have warmed the mixture to a temperature of 70° C. the emulsion clears; in other words, the amounts of phenol and water with which I started dissolve completely in each other. I could actually add any amount more of either of the two, at this temperature, without their separating out.

Above the "critical" temperature, phenol and water are miscible in all proportions. For this experiment I have, of course, not chosen indifferent amounts of phenol and of water, but a concentration of about 36 percent of phenol. This represents the "critical" concentration of phenol in water, the significance of which I cannot discuss further here.

While I have been talking, the white emulsion of phenol and water has given way to a clear solution. We have before us now a molecularly dispersed solution of the phenol in water. But the phenomenon to which I wish to direct your particular attention is to be observed when we begin to cool this system, either by shaking the flask in the air or by placing it under the water tap. You can see in advance that as I reduce the temperature a separation of the system must again occur, for the solution phenomena that you have observed are entirely reversible. The solution has now cooled somewhat, but if you observe closely you note at the same time that it has also changed in appearance. What was formerly a completely colorless liquid shows now a bluish yellow *opalescence* entirely identical with the opalescence of an egg white solution, or a highly dispersed mastic colloid. The opalescence increases as the mixture cools. The similarity between the opalescence in our phenol-water mixture and the opalescence of typical colloids compels the conclusion that we have before us a separation of the phenol in the water in colloid form. In fact, consideration of the problem compels the conclusion that such a colloid state must be passed through in the course of the separation in such a system; and it only becomes a question as to whether we are able experimentally to maintain or "stabilize" this colloid state, when reached, long enough to be able to examine it carefully. We begin with a temperature at which we have to do with a molecular division of the two substances in each other and end with a lower one at which we have to do with a coarsely dispersed, or even non-dispersed, mixture of phenol and water. Evidently somewhere between these two extremes we pass through the colloid realm and the opalescence of the mixture before you renders it probable that we have it before us now. Ultramicroscopic investigation furnishes direct proof *that this opalescent critical fluid mixture is really one in which the divided phase has colloid dimensions.*[1]

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[1] The analogy between critical fluid mixtures and colloid solutions was first pointed out by D. Konowalow, Drudes Ann., **10**, 378 (1905). Without knowledge of his work I characterized these systems as emulsoids in 1906. See Koll.-Zeitschr., **1**, 335 (1907); Grundriss der Kolloidchemie, 1. Aufl., 102, Dresden, 1909; W. von Lepkowsky, Zeitschr. f. physik. Chem., **75**, 608 (1910).

Other, and, in part, startling analogies are discoverable between the properties of critical fluid mixtures and the properties of emulsoids, more particularly of the solvated emulsoids of the type of gelatin. Unfortunately, I cannot demonstrate all these to you. Critical liquid mixtures frequently show, for example, the properties of *foaming*, which are not observable in molecular solutions of these materials as obtained at higher temperatures.

FIG. 30.—Viscosity of a critical fluid mixture.

But more important still is the fact that with the appearance of the opalescence there occurs also a remarkable *increase in the viscosity of the mixture.* As you know, the viscosity of every liquid increases on cooling, but in the case of critical fluid mixtures, this increase in viscosity is abnormally great in the regions of the critical temperature, and, after the opalescence region has been passed, the viscosity falls again even though the system, as a whole, is then at a lower temperature than before.

If the viscosity of the phenol-water mixture before you is measured while being cooled, there is first observed, at the temperature at which opalescence appears, a sudden increase in the viscosity, as shown in Fig. 30. The maximum viscosity at this temperature is much above the viscosity of either of the two pure components. If the mixture is further cooled, the opalescence disappears, giving way to a white turbidness characteristic of the relatively coarse dispersoids. This is the state that the phenol-water mixture has now assumed (demonstration). If we measure the viscosity of this white emulsion, we find it considerably less than that of the opalescent colloid mixture. Paralleling this appearance and loss of opalescence we find the viscosity attaining a maximum in the realm of colloid separation, and then falling again as shown in Fig. 30.

To give you some conception of the quantitative side of these changes in viscosity, let me read you a few figures that have been observed in the carefully studied critical fluid mixtures of isobutyric acid-water. While the viscosity of pure water at 20.12° C. has a value of 1.1245, and that of pure acid at 20.08° one of 1.983, the viscosity of a critical mixture of 59.93 percent acid has a value of 3.677 at 20.99°. The changes in viscosity become still more evident when the logarithms of viscosity are compared with the temperatures, as in the accompanying Fig. 30.

This analogy between the behavior of critical fluid mixtures and that of solvated emulsoids throws light upon some of the changes that take place in the process of gelation. The sudden increase in viscosity of a critical fluid mixture when cooled is analogous to the stiffening of a solvated colloid and the process of gelation. There occurs in gelation, as in critical fluid mixtures, a *separation* of the colloid — a conclusion that may be verified by ultramicroscopic and other methods.[1]

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[1] See Wolfgang Ostwald, Grundriss der Kolloidchemie, 1. Aufl., 347, Dresden, 1909. The ultramicroscopic phenomena predicted here were subsequently discovered and developed by R. Zsigmondy, W. Menz, W. Bachmann and others. See their papers in the Kolloid-Zeitschrift.

§9.

In the gelation of colloids, such as gelatin, agar, albumin, etc., a separation into *two* well-marked phases takes place. As in phenol-water mixtures, there are formed, first, a *concentrated* phase rich in colloid and containing little water, and second, a *dilute* phase rich in water and relatively poor in colloid. This is true of those colloids at least which in the presence of sufficient water *always* have the tendency to pass over into the liquid state and which have never been observed in solid, for example, crystalline form. It is possible, however, for phases which originally separate out as fluid droplets to yield later tiny solid *crystals*. This occurs in the course of time in the gelation of silicic acid and certain soap solutions for instance. Both silicic acid and certain soaps originally give rise to gels which look much like the ordinary emulsoid gels, yet they are distinguishable from these by not possessing much elasticity. But that which is common to all these gelations is the phenomenon of separation; in other words the *decrease* in the degree of dispersion of the whole system on the one hand, and the distribution of the dispersion medium in unequal concentration in the two phases on the other.

It might now be urged against this comparison that in a critical fluid mixture the separation of the two phases, when the dispersed state is reached, is not *maintained*, but that a coarsely dispersed or even non-dispersed mixture of the two liquids ultimately comes to pass. But even this has found its analogue in jellying colloids. GRAHAM first observed it and his findings have been commented upon many times since, though little attention has been paid to these comments.[1]

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[1] I have during the past years made many experiments upon syneresis, without, however, having found time to bring them to a conclusion and to publish them. Not only the term itself but all reference to syneresis seems to have disappeared from the literature. None of the ordinary text-books of colloid chemistry, for example, touch upon it. I hold it and its study as extraordinarily important, as may be inferred not only from what is said above, but from some paragraphs which are to follow. The phenomena

When any gel is left to itself for a number of hours or days, protected not only against infection with microorganisms, but also against evaporation, *a separation into two phases takes place.* Every bacteriologist working with solid media has observed this. Agar slants, for example, squeeze off fluid droplets in the course of time, which coalesce to form considerable volumes of liquid. The liquid is usually called condensation water, a designation liable to confuse one, for the liquid is not the product of condensed water vapor, but is actually *secreted* by the colloid. The liquid is, moreover, *not pure water but a solution of all the constituents of the gel in both colloid and molecular degrees of dispersion.*[1] *Only these constituents are present in a different, that is to say lower, concentration.* The "serum" given off is therefore in reality a second colloid solution secreted by the concentrated colloid, the whole being quite analogous to the separation phenomena noted in critical fluid mixtures. GRAHAM called this separation *syneresis.* It is strange how little this theoretically and practically important phenomenon has been studied.

I have never seen a gel which does not show syneresis. Not only do agar and gelatin (in which the amount of the fluid given off increases with decreasing concentration of the colloid) show this behavior, but so do starch, silicic acid (the concentrated gels of which give off more fluid than the dilute), rubber, collodion, cellulose, the gelatinous sodium chlorid which I have already shown you, etc.

I show you here the syneresis of a gelatin, a silicic acid and a viscose gel (demonstration). In order to prove that

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of syneresis not only cover, in my mind, a group of changes in state coördinate with the phenomena of swelling and of gelation, but they are possessed of possibilities for application to scientific and technical problems of the greatest importance. See, in this connection, the last two lectures in this volume.

[1] According to unpublished experiments, I demonstrated the presence in the syneretic serum of the colloid responsible for the gelation in the fluids expressed by silicic acid, gelatin, agar, starch, sodium chlorid and polymerized cinnamic ethyl ester. The degree of dispersion of the colloid in the expressed fluid is, naturally, always much greater than in the gel.

the fluids which have been expressed are not simply water or salt solutions but contain colloid material as well, I shall pour off a part of the "serum" from each of the two flasks. To the liquid from the gelatin flask I add a few drops of dilute hydrochloric acid and some tannin. The white cloud which develops betrays the presence of gelatin. To this second test tube I add some copper sulphate; the precipitate of copper silicate formed shows that the "serum" in this case also contains colloid material.

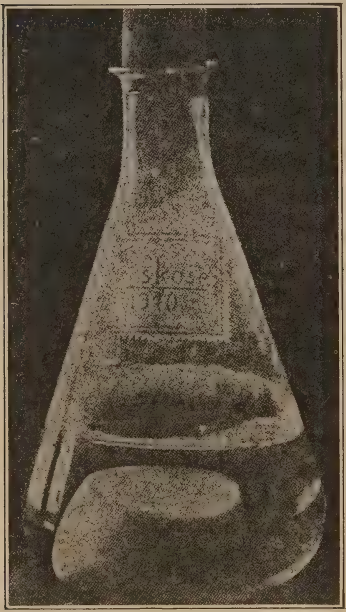

Fig. 31. — Syneresis of a viscose gel.

The syneresis of a viscose gel (see Fig. 31) is particularly striking because of its extraordinary extent. About two thirds of the original volume of the gel separates itself in liquid form from a very solid cake. The separation, of course, takes time, — in this instance several years.

This phenomenon of syneresis, therefore, closes the ring of analogies between the behavior of critical fluid mixtures and that of hydrated colloids. Let me add that microscopic study of colloids to which dehydrating materials have been added supports the assumption that separation occurs in "droplet" form in the process of gelation,[1] and that this phenomenon is analogous to that observed when benzol separates as a coarse emulsion from water.

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[1] See especially the studies of O. Bütschli and W. B. Hardy discussed by Wolfgang Ostwald, Grundriss der Kolloidchemie, 1. Aufl., 350, Dresden, 1909.

§10.

But the gel state may be reached not only by allowing a liquid mixture to set, but by allowing a solid to absorb a dispersing medium. As you know, a disc of solid gelatin goes over into a jelly when it is thrown into water. Differently expressed, the gelatin *swells*. Such swelling may be observed in other colloids than gelatin and with dispersion media other than water. Thus, rubber swells in benzol, collodion in alcohol-ether, etc. Let me illustrate some of these swellings and in connection with them call your attention to the more important properties of the observed colloid changes in state.

I have here a disc of ordinary carpenter's glue, the under half of which has lain in water over night (demonstration). You observe the considerable increase in volume of the immersed portion, and, at the same time, an interesting optical change. The swollen half is white and *turbid* while the unswollen portion has kept its brown color and relative transparency. The immersed portion has yielded a jelly with corrugated surface, well-marked elastic properties, etc. (demonstration).

The increase in volume when materials swell can be demonstrated even better in the following fashion. I have here some very thin and but slightly vulcanized rubber foil such as dentists and surgeons use. I have cut from it a pantaloon-shaped strip as indicated in *A* of Fig. 32. One of these two divisions we will now permit to swell in order that we may compare its change in volume with that of the unswollen portion. To do this one-half of the divided strip is left hanging outside a test tube while the other half is tucked inside. I next carefully fill the test tube with cumol, or benzol. Since the swelling, like all other colloid changes, takes time, I set the tube aside for a few minutes.

The production of a gel through swelling necessitates the existence of certain physico-chemical relationships between the material undergoing swelling and the liquid producing it. Of the reasons for this we know but little as yet. Gelatin swells in water but not in benzol; vulcanized rubber in benzol but not in water. Sometimes a definite temperature is necessary in order that swelling may take place. Starch, for example, does not swell at room temperatures but does at higher ones; potato starch begins to swell between 57° and 58° C. This swelling temperature can be determined very accurately[1] by measuring the viscosity of a starch suspension while it is being heated. As soon as the proper temperature is reached, a sudden great increase in the viscosity is noted which becomes particularly evident if the logarithms of the viscosities are compared as in Fig. 33.

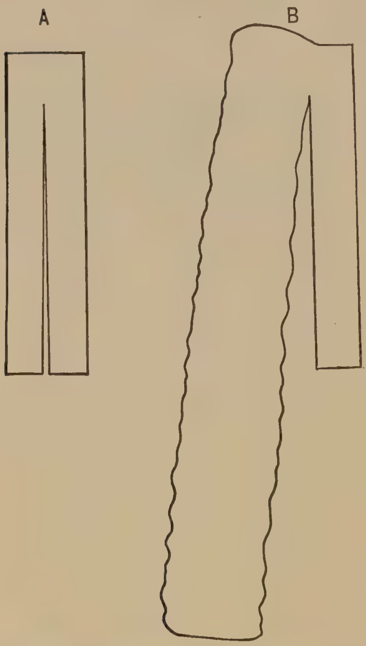

FIG. 32. — Swelling of soft rubber.

It is an interesting fact that certain crystals, like those of albumin, show well-marked swelling. Inorganic solids also swell, as do even metals like sodium and potassium in the presence of liquid or gaseous ammonia. At low temperatures all these substances swell considerably without losing their general forms. When the ammonia is driven off, the pure solids or metals are again obtained. On the other hand, when the ammonia is allowed to act long enough all these substances liquefy, yielding at first a doughy, highly viscid mass which, in most cases, then goes over into a

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[1] See WOLFGANG OSTWALD, Koll.-Zeitschr., **12**, 218 (1913); Kleines Praktikum der Kolloidchemie, 38, Dresden, 1920. Regarding optical methods of determining these swelling points, see M. SAMEC, Kolloidchem. Beihefte, **3**, 129 (1911).

colloid solution.[1] The same thing happens when acacia or rubber swells. Under the influence of the material producing the swelling and especially at higher temperatures, the swelling gradually gives way to colloid solution. In some colloids, as in acacia, the temperature necessary for this lies so low that at room temperature only solution phenomena may be observed. But at 0° C. the particles of acacia show the normal phenomena of swelling.

Fig. 33. — Changes in viscosity during the hydration of starch.

Swelling can occur not only in liquids but also in vapors. But there is a difference, under ordinary experimental conditions, not only in the rate at which the swelling is brought

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[1] Regarding the swelling of metals and their salts in ammonia and its probable colloid nature, see Wolfgang Ostwald, Kolloidchem. Beihefte, **2,** 437 (1911) where references will be found to the literature.

about, but in the maximum amounts of liquid that may be taken up by the swelling substances in the two media. A gelatin disc, for example, takes up less fluid in an atmosphere of water than in water itself.

While I have been speaking our experiment on the swelling of rubber has made progress, and so I now withdraw the immersed half from the test tube. As you see (Fig. 32, *B*), the amount of swelling even in these few minutes is enormous. The immersed half is at least half again as long and as broad as the unimmersed. Moreover, the rubber in swelling has changed in some of its properties. As I shake the strip you catch a sound not unlike that heard when writing paper is rattled. Please note the relatively great velocity at which these changes in state have taken place. It is a matter of enormous interest in certain biological problems to which we shall return later.

§11.

I should like now to call your attention to another swelling phenomenon which illustrates swelling in vapor and which also takes place with incredible speed. The experiment illustrates the close association between swelling and certain *kinetic* processes. I have here some thin leaves of colored gelatin which will recall your childhood days. I take one that has been cut and decorated to represent a fish, and lay it upon a piece of filter paper. When I breathe upon it you observe that the gelatin leaf immediately bends or even curls up and jumps upward (demonstration). Perhaps you think that the movement is merely the mechanical result of my having blown upon the leaf. To meet this criticism I have fastened a gelatin leaf into a ring stand. When I breathe upon it, the leaf bends away from me (demonstration). It *remains* for a time in the new position and only slowly returns to the old. This proves that the movement is really brought about through an increase in the volume of the gelatin on the side of the leaflet which has been breathed upon, in other words, through swelling. But the swelling soon disappears, for the absorbed water evaporates rather quickly from so large a surface.

This experiment demonstrates vividly the rapidity and the enormous value of swelling phenomena. It is for this reason that they serve us in the making of certain scientific measurements. The principle is used in the well known hair hygrometer in which the change in the length of a stretched human hair through the humidity of the air constitutes the principle employed for measuring the latter. Why blond hair works better for these purposes than dark hair has not yet been settled scientifically.

§12.

Of great interest is the effect of the *addition of various substances* upon swelling. Electrolytes and non-electrolytes are known which not only favor but also inhibit swelling. Among the most powerful of those which increase the swelling of such colloids as are capable of absorbing water are acids and alkalies. Gelatin and fibrin, for instance, in the presence of acids or alkalies will absorb several times as much water as when these are absent. Cyanids, iodids, chlorids, etc., also favor colloid swelling in certain concentrations, while sulphates, citrates, phosphates, alcohol, sugar, etc., do the opposite. On the other hand, when salt and acid are used in combination, the addition of salt usually brings about a decrease in swelling, even though the salt is of a kind which alone leads only to increased swelling.

To demonstrate these effects I have here a series of dishes containing water, acid, alkali, potassium iodid, calcium chlorid and magnesium sulphate. Into each of them has been dropped a gelatin disc of standard weight (demonstration). To render the discs readily visible, a trace of *colloid* dye, namely, congo red, has been mixed with the gelatin. Had a molecularly dispersed dye been used it would, of course, have diffused out of the gelatin while this was swelling. The gelatin discs have been in these solutions some twenty-four hours and, as you observe, the way in which the different substances have favored the swelling is as follows:[1]

acid, alkali, potassium iodid, calcium chlorid, water, magnesium sulphate.

The disc in the acid solution is already swollen to twice the size of that in the pure water.

I should like briefly to emphasize that, in the process of swelling, considerable heat is set free and that considerable quantities of energy suffer conversion. Swelling seeds, for example, can lift great weights. In a skull filled with dried peas and immersed in water, the swelling peas burst the bones of the head apart. The old Egyptians used these swelling phenomena for quarrying purposes when they drove dry wood wedges into the rocks and then made the wedges swell by pouring water upon them.

§13.

Were you now to ask me what are the internal changes in state which permit a solid body and a liquid or vapor to become a jelly, I could not give you a short and simple answer. I can only emphasize the following. There is, in the first place, a great similarity between a swelling system and a syneretic emulsoid system. In the swelling of the colloid, as I need to emphasize at this time, a small portion of the swelling substance always passes over into a colloid solution. In syneresis, on the other hand, we have also to do with a concentrated, practically solid phase covered by a dilute colloid solution. Swelling, in other words, represents the reverse of syneresis. The whole is analogous to

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[1] These gelatin discs are prepared by pouring a concentrated gelatin solution upon a glass plate. The gelatin is allowed to set, after which it is cut into squares which are then dried and weighed. See WOLFGANG OSTWALD, Kleines Praktikum der Kolloidchemie, 82, Dresden, 1920. For demonstration purposes the discs are immersed in 1/20 to 1/10 normal hydrochloric acid or sodium hydroxid. Half normal potassium iodid, 1/8 normal calcium chlorid, or highly concentrated (saturated) magnesium sulphate solution may be used to demonstrate the salt effects.

what may be observed when a gelatin gel, which has been kept at a low temperature and which shows the phenomenon of syneresis, is again exposed to a higher temperature. In both instances a pronounced diphasic, non-dispersed system gives way to a simple dispersed system, namely, the gel. In the process of swelling, two macroscopically differentiated systems give rise to a single dispersed one.

The power of a solid body to yield a gel through swelling seems to be connected with the presence of a definite structure. Through the extensive and masterful studies of O. Bütschli, G. Quincke and others, it has been proved that microscopic and ultramicroscopic discontinuities — in the form of meshes, cells, foams, honeycombs, etc. — are widely distributed in nature. Not only do those solids which are capable of swelling show these structures, but also many of the inorganic crystals as those of congealed sulphur and the so-called skeletons of potassium permanganate and ammonium chlorid. This finding is in harmony with the fact cited above that these crystalline substances show a behavior closely allied to the phenomena of swelling. That metals may show such structure is well known to every metallurgist.

If we believe with O. Bütschli, G. Quincke and others that structure is necessary before swelling can occur in a solid, then the process of swelling consists, in the first place, of an increase in the degree of dispersion of these systems. This increase is then analogous to the increase in degree of dispersion as observed in the reversion, through heat, of a syneresis, or of the effects of age in a colloid. The coarser structure of the solid is, as it were, broken up; in other words, coarse aggregates are divided into the primary particles of which they are composed. As N. Gaidukow has found, the ultramicroscopic particles of a gel become smaller in the process of swelling, or at least lose their highly refractive character.[1] But in the process of swelling there

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[1] See N. Gaidukow, Dunkelfeldbeleuchtung und Ultra-mikroskopie in der Biologie und in der Medizin, Jena, 1910; Koll.-Zeitschr., **6**, 260 (1910).

occurs another change which may, under certain circumstances, actually run counter to the increase in dispersion. The individual particles absorb the medium in which they are swelling; they become *solvated.* This *increases* the size of the particles and so fluid droplets may be formed. The two changes, in other words, the combination of increase in degree of dispersion with a change in the type of the dispersed substance from the side of the solid to that of the fluid, seem most characteristic of the process of swelling. Accordingly, *the process of swelling represents the reverse of syneresis.* These statements cover what is best established at this time regarding the changes of a disperso-chemical nature that occur in the process of swelling.

§14.

Let me add a few words regarding the properties of *gels.* Gels show in interesting fashion the properties of *both* solids and liquids. Thus, even when holding 98 percent or more of fluid, they may still show maintenance of form and elasticity. They may be cut or broken into pieces that hold their shapes, and may be bent and regain their original form in the same way that solids do (demonstration). On the other hand gels show the properties of liquids. Thus, they flow when subjected to slow deformation, as when a large two percent gelatin cake assumes the shape of the conical vessel into which it is introduced. Unfortunately this experiment takes too long to permit me to demonstrate it to you. I can demonstrate to you this double-sided behavior as determined by the rate at which mechanical deformation is brought about in a system which, while not belonging to the typical gels nevertheless belongs to a closely associated group of systems, namely, the *doughs.* I have in this mortar several grams of ordinary potato starch to which I shall, while using the pestle, add enough water to make a dough. You observe that the material can be poured out of the mortar upon a glass plate in a continuous stream (demonstration). There is formed a very large liquid "drop." When, however, I try to stir this mass with a spatula something happens which in no wise agrees with the physical constitution of a liquid (demonstration). My rapidly moving spatula drives before it lamellæ possessed of sharp edges, in other words, masses which show all the characteristics of solid bodies. If I wait a moment the sharp edges disappear, they become rounded and the lamellæ again "run together." I can also take a large mass of this dough and by handling it *rapidly* knead it into a ball (demonstration). But when I place this ball upon a plate it liquefies at once under the influence of its own weight. If I had kept the ball in my hand the material would have flowed through my fingers. You observe then, that depending merely upon the *rate* of the mechanical manipulation a structure may behave at one time like a liquid and at another like a solid.

The free movement which molecularly dispersed particles show in gels is another argument in favor of their fluid nature, a phenomenon which we observed in our first lecture when discussing diffusion in gels. How now can we understand this remarkable combination of solid with liquid properties?

Our previous remarks led to the conclusion that gels are systems which, on the one hand, are more coarsely dispersed than the liquid sols from which they are prepared, while they are, on the other hand, more highly dispersed than the solids from which they may be prepared through swelling. The gels evidently occupy a middle position, so far as degree of dispersion is concerned. Furthermore, the degree of dispersion in a gel may vary steadily from values approximating those of the coarse dispersions to those of the colloids. Through not considering this fact much useless debate has arisen. It is, for example, of no purpose to ask whether gels have *only* a microscopic or *only* an ultramicroscopic structure, since both may be found not only in different gels, but at one and the same time in any gel. As O.

Bütschli assumed and as proved in the ultramicroscopic investigations of R. Zsigmondy and W. Bachmann among others many gels have a dual structure. They may contain ultramicroscopic particles which, in their turn, may coalesce to give rise to structures of microscopic dimensions. This behavior is common and entirely in harmony with the theory of gelation sketched above.

A gel may, moreover, actually have a structure of microscopic dimensions without this being recognizable by microscopic or ultramicroscopic means. As I emphasized before, a difference in degree of refraction is necessary to permit optical differentiation. In highly solvated colloids such differences may not appear. Nevertheless, a gel *remains* a gel even though it *appears* optically homogeneous, as in the case of gelatin. Sometimes through treatment with alcohol or other dehydrating agents, we can bring about refraction differences in such gels, which then make possible optical differentiation of structure. By the use of such agents we may change quantitatively the characteristic properties of a gel, as its maintenance of form, its elasticity, its permeability to molecular dispersoids, etc., but we do not change its qualitative character. The fact remains that the degree of dispersion of a gel is less than that of the liquid "solvent" and higher than that of the solid from which it was derived. Between these limits the degree of dispersion may assume any value. When gels are produced, as is most commonly the case, by allowing colloid solutions to cool, we may say that the characteristic structure of these systems depends upon the size of the "primary" colloid particles composing it, which means that *it must at least lie near the realm of colloid dimension or actually within that of microscopic visability.* Whether in such gels the possibility always remains of recognizing these "primary" colloid particles (as by ultramicroscopic means) is a question of secondary importance, which, in different cases and with different degrees of dispersion and of solvation, may have different answers.

But just as the degree of dispersion may vary, so also may the *type* of the elements composing the gel. In gels produced by swelling, I do not know of an instance in which the dispersed elements are solid or crystalline in character. They are, apparently, always liquid. There are, however, cases in which an ultimate separation in solid crystalline form occurs. Thus, the gelatinous precipitates of metal hydroxids may after a time lose their typical gel properties and become crystalline. This can also be noticed in silicic acid gels which, in the course of time, become brittle and break up into inelastic masses. The belief that we deal in this instance with the formation, initially, of an emulsoid gel which changes later to a suspensoid gel is borne out by recent Röntgenological studies which show that a normal silicic acid gel has no crystalline structure while one which has been heated, has.[1] A marked elasticity is usually more noticeable in emulsoid than in suspensoid gels, even when in the latter case the crystalline elements, through union with each other and similar phenomena of agglomeration give rise to the mechanical circumstances necessary for the attainment of high elasticity values.

§15.

I leave this somewhat theoretical discussion in order to acquaint you with some further properties of gels (demonstration). Since gels are permeable to molecular dispersoids, chemical reactions may be permitted to occur in gels by allowing two molecularly dissolved substances to diffuse toward each other in a gel. If I half fill a test tube with a gelatin solution containing some potassium bichromate and, after the gelatin has set, pour some silver nitrate solution upon it, the two dissolved substances diffuse into each other. The silver nitrate, particularly, will diffuse downwards into the gel, as I have previously demonstrated to you. But here the silver salt meets the bichromate and, exactly as in

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[1] S. Kyroponlos, Zeitschr. f. anorg. Chem., **99**, 197, 249 (1917).

free diffusion, a precipitate or silver chromate is formed, the amount of which increases as the diffusion progresses. But something happens in this reaction as it occurs within a gel which does not take place when diffusion is "free." Were no gel present, the amount of the precipitate would increase progressively with the course of the reaction. But in the presence of the gel, when the conditions for the experiment are properly chosen, there occurs a *periodic* precipitation. In the test tubes that I pass around, instead of a continuous column of silver chromate, you observe a series of rings or layers of this substance between which the gel is practically colorless, indicating the absence of any precipitated silver salt.

FIG. 34. — Periodic precipitations of lead chromate according to E. HATSCHEK.

Similar periodic precipitations may be obtained by allowing other reactions to occur in gels. In Figs. 34 and 35 are shown some beautiful precipitates of lead chromate prepared by E. HATSCHEK.[1]

I can demonstrate this phenomenon of periodic precipitation still better by utilizing a projection apparatus and some plate preparations. In these the gel containing one salt has been poured upon a glass plate. After setting, the second reacting solution has been dropped upon it in one spot or has been painted upon the gel in the form of a ring (Figs. 36, 37 and 38). You observe in Figs. 36 and 37 how the spot made by the original drop is surrounded by a vast number of dark rings marking the periodic precipitations of

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[1] See E. HATSCHEK, Koll.-Zeitschr., **8**, 193 (1910); **9**, 97 (1910); **10**, **77**, 124, 265 (1911); **14**, 115 (1914); also the many papers of R. E. LIESEGANG, E. KÜSTER and others in the Kolloid-Zeitschrift.

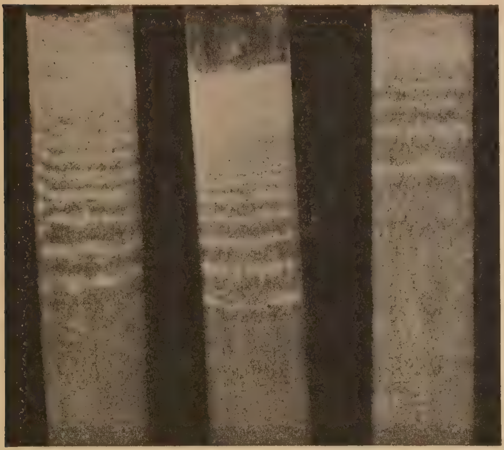

FIG. 35.—Periodic precipitations of calcium carbonate according to E. HATSCHEK.

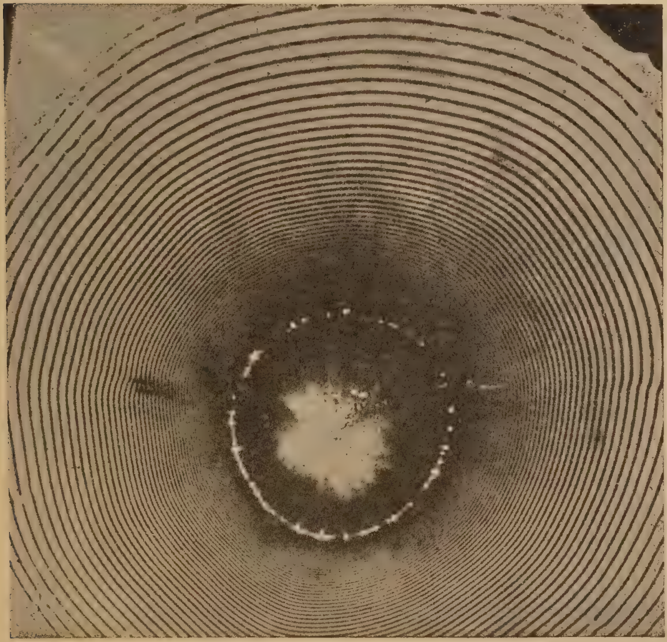

FIG. 36.—Periodic precipitations of silver chromate in gelatin according to R. E. LIESEGANG.

silver chromate. Fig. 38 shows the results when a ring is painted upon the gelatin.

These periodic precipitations in gels are known as LIESEGANG rings in honor of their discoverer. The theory of their origin is still a matter of debate. Even the pretty and long accepted explanation of WILHELM OSTWALD seems inadequate in the light of newer studies.[1] Should any of you like to make some of these interesting preparations for yourselves, let me emphasize that the phenomenon is obtained in good form only when definite concentration relationships between the materials necessary for the formation of the precipitates are maintained.[2]

FIG. 37. — Silver chromate rings in gelatin.

Fig. 39 illustrates another interesting property of gels.

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[1] See especially the more recent publications of E. HATSCHEK in the Kolloid-Zeitschrift.

[2] Instructions originating with R. E. LIESEGANG which I have found to give splendid results read as follows: a gel is prepared from 4 grams of gelatin, 120 grams of water and 0.12 gram potassium bichromate. The silver nitrate solution contains 8.5 grams of the solid salt in 100 cc. of water.

When gelatin is painted upon a glass plate and is then allowed to freeze, the water in the gel crystallizes, under proper experimental conditions,[1] to form the well-known

Fig. 38. — Silver chromate rings in gelatin.

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[1] Following the method of R. E. Liesegang (Prometheus, **25,** 369), glass plates are covered with a thin layer of a 2 to 10 percent gelatin solution and before these have dried they are exposed to cold. In order to obtain the best pictures, it is well to keep the preparations for some time in the cold. The ice evaporates after about a day. The gelatin lamellæ dried

frost figures. In the process, the water naturally separates from the gelatin or pushes it aside. If the cooled plate is now thawed, the ice crystals disappear but the gel maintains the shape given it by the frost figures. In this way negatives of the ice crystals may be obtained which may be lasting and which at times are remarkably pretty. The illustration shown in Fig. 39 as well as the method of producing such frost pictures is the work of R. E. Liesegang.

Finally, I wish to show you a third set of preparations which will serve to demonstrate to you the tremendous energy changes incident to the changes in state of gels. When a gelatin solution is dried upon a glass plate, as in an oven at 100° C., the gel contracts. But at the same time it sticks so fast to the glass that large shell-shaped pieces are torn off the surface of the glass as shown in Fig. 40. I have learned that such methods in which common glues or ising-glass are employed as the active colloids, are used technically in the manufacture of certain types of opaque window glass.

§16.

I need to hasten on to the consideration of some further changes in the state of colloid systems. Since the earliest days of colloid chemistry, many studies have been made of the *coagulation* of colloids; in other words, of the decreases in degree of dispersion which lead to the formation of microscopic and macroscopic dispersoids. It may be said fairly that our so-called theories of the colloid state, as proposed from time to time, have all centered about the explanations that they have offered of the process of coagulation. There have been proposed electrical, chemical and mechanical theories of the colloid state by which were usually meant corresponding theories of the process of coagulation. Each of these attempted to make one of these principles either

in this fashion then maintain their structure even if after this treatment they are brought back to room temperature.

FIG. 39. — Artificial frost pictures in gelatin.

the only factor or at least the most important factor in the process of coagulation.

In considering the forces that are active in the *destruction* of the colloid state through coagulation, I would like to have you recall what was said in our first lecture regarding the production of colloid systems. We discovered then many methods and many types of energy by which we could bring about a change in the degree of dispersion. We may, in consequence, expect a similarly great number to be active in the induction of coagulation.

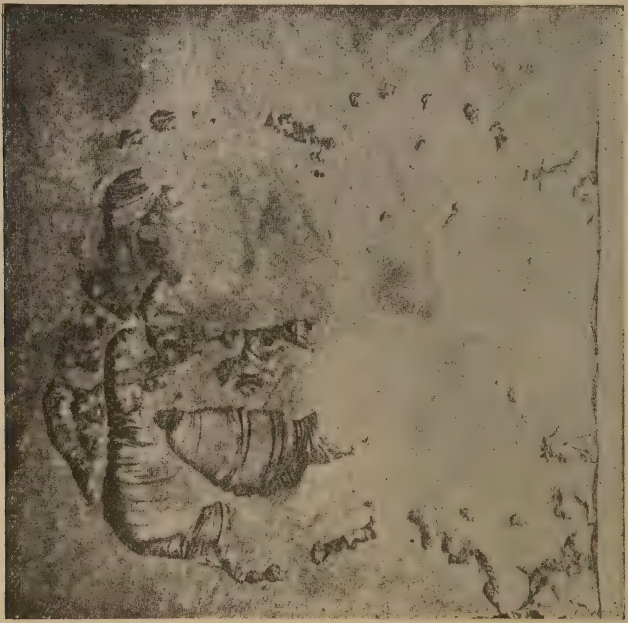

FIG. 40. — Chipping of a glass plate brought about by the drying of gelatin.

We need not, therefore, expect to find of dominant importance some one method of coagulation, as we thought formerly, *but a whole series of different although coördinated ones.* As a matter of fact, any attempt to classify the different methods of inducing coagulation shows present in all of them a mixture of mechanical, electrical and chemical forces, which together lead to the radical decrease in degree of dispersion that we term coagulation.

To enter for a moment into details, it may be said that in the coagulation of *suspensoids* through electrolytes, electrical phenomena play a chief role even though not so exclusive a one as has been thought.[1] Disperse particles having opposite charges are particularly liable to precipitate each other. Thus the negatively charged metal sols are precipitated through very low concentrations of acids, that is, by positively charged hydrogen ions. Other cations, like those of the neutral salts, act similarly. On the other hand a positively charged sol like that of iron hydroxid is precipitated most easily by bases, in other words, by negatively charged hydroxyl ions. In the case of this colloid the anions of the neutral salts are particularly effective in producing precipitation. The great influence of the electrical factor in all these coagulations is strikingly evidenced by the importance of the valence of the precipitating ions. The coagulating power of different salts for a gold sol increases in the order:

$$NaCl \qquad MgCl_2 \qquad AlCl_3$$

while for iron hydroxid it increases in the order:

$$NaCl \qquad Na_2SO_4 \qquad Na_3(C_6H_5O_7).$$

Much smaller quantities of the salts yielding ions of high valence are necessary, therefore, to bring about a radical decrease in degree of dispersion, than of those yielding ions of lower value.

Oppositely charged colloids precipitate each other; thus colloid gold precipitates colloid iron hydroxid, and congo red precipitates aluminium hydroxid (demonstration). Precipitation in these instances is apparently brought about

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[1] Valence is therefore not always or alone responsible for the precipitating power of an electrolyte; see Wolfgang Ostwald, Koll.-Zeitschr., **26**, 28, 69 (1919).

through electrostatic attraction of the particles, neutralization of their charges and coalescence. It is interesting to note how very low may be the concentrations of electrolytes which suffice to bring about a precipitation of suspensoids. Ordinary india ink, for example, may not be diluted with tap water, for the salts contained in this water suffice to precipitate the ink.

Coagulation of hydrated emulsoids through electrolytes represents a much more complex problem. We expect this for we know that in the precipitation of a protein solution through neutral salts, *two* changes must occur side by side. There must first occur a dehydration (which in itself leads to an increase in degree of dispersion), and then a coincident, or subsequent coalescence of the particles into coarsely dispersed aggregates. The importance of the hydration element is strikingly evidenced by the fact that in order to render precipitation possible relatively large amounts of salt are required. Hydrated emulsoids are for this reason *more stabile* than suspensoids, which we found above so very sensitive to low concentrations of different salts. The dehydrating effects of neutral salts, as well as the dehydrating effects of alcohol, etc., are probably *not* primarily electrical in nature, even though the electrical charge[1] of the substances used may not be without influence. The dehydrating agents follow their own physico-chemical laws, which, however, are still but little understood. Electrical and non-electrical processes are, therefore, associated in the precipitation of hydrated emulsoids through neutral salts. Perhaps the matter is best illustrated in the studies of W. PAULI, which show the whole salt, in other words, both ions, to play an important part in coagulation. The effects

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[1] See particularly the papers of WOLFGANG PAULI and his pupils in the Biochemische Zeitschrift, the Kolloid-Zeitschrift and the Kolloid-chemische Beihefte. See for example WOLFGANG PAULI, Koll.-Zeitschr., **7,** 241 (1910); **12,** 222 (1913); H. HANDOVSKY, Koll.-Zeitschr., **7,** 183, 267 (1910) as well as the monograph of PAULI, Kolloidchemie der Eiweisskörper, Dresden, 1920.

of any salt represent the algebraic sum of its constituent ions, the effects of which may be additive or antagonistic. The non-electrical nature of dehydrating and coagulating effects is most clearly to be observed in electrically neutral or but weakly charged emulsoids, while in the heavily charged, such as acid or alkali proteins, the electrical effects again come to the front. In the precipitation of acidified (positively charged) proteins, the coagulating power of the neutral salts follows the well-known HOFMEISTER series. Anions follow the order:

chlorate, nitrate, chlorid, acetate, sulphate, tartrate;

the bases, the order:

magnesium, ammonium, sodium, potassium, lithium.

These series are reversed when alkalinized protein instead of acid protein is used. The important rôle of the valence of the ions largely disappears as soon as neutral albumin is used, though this is still capable of being precipitated by neutral salts, according to the experiments of W. PAULI. These facts prove that in this case the electrical relationships play only a secondary rôle and that this type of coagulation may perhaps best be designated as *coagulation through withdrawal of solvent.*

§17.

Interesting phenomena are observed when the coagulation of mixtures of suspensoids with hydrated emulsoids is studied. The greater stability of the emulsoid fraction is then carried over to the suspensoid fraction which, in consequence, becomes less sensitive to concentrations of salt which previously coagulated it. We say the emulsoids exercise a *protective action* upon the suspensoids and explain the phenomenon by assuming that the fluid emulsoid droplets surround the suspensoid particles, or in some way combine with them — a view well supported, for example, by ultramicroscopic observations. The protective action is shown even by traces of emulsoids, another fact in harmony with the explanation just given, for theoretically only very little emulsoid material is necessary to surround a suspensoid particle.

Much use is made in scientific and technical colloid chemistry of this protective action of the emulsoids. Thus, the presence of traces of gelatin enables us to produce more concentrated and more highly dispersed sols than can be produced in pure dispersing media alone. The effect of tannin in the production of a highly dispersed red gold of the type I showed you in my first lecture depends in good part upon such a protective action. The tannin not only acts as a reducing substance, but *at the same time* as a protective colloid. The presence of a protecting colloid is also of advantage because it makes possible the evaporation of suspensoid sols to dryness. Because of the spontaneous solubility of the protective colloid the dried material, when thrown into its solvent, can be brought back into a state of colloid solution, *the suspensoid fraction retaining under these circumstances its original high dispersion value.* I show you here a number of such "dried hydrosols" (demonstration). They are, as you see, mostly dark colored scales which are readily soluble in water (demonstration).

§18.

In addition to the methods of coagulation brought about through the addition of different substances, others are known in which *radiant energy*, as from radium emanations, is active. Coagulation may also be brought about through exposure to light, through shaking with charcoal, with Fuller's earth, or with other powders, and through the addition of non-miscible liquids. Thus, many colloids, including the proteins, may be separated almost completely from their dispersion media by being shaken for long periods of time with benzol or petroleum. Moreover, when egg white is beaten to a foam, a part is regularly coagulated in the walls enclosing the air bubbles.

A decrease in degree of dispersion to the point of inducing coagulation can also be brought about through centrifuging, etc. These belong to the mechanical methods of producing coagulation. Certain details of the way in which these different methods produce their effects will be discussed later.

§19.

The reverse of coagulation, namely, *peptization*, may also be brought about by the most diverse chemical, electrical and mechanical means. Coagulated gels, for instance, may again be brought to a state of colloid dispersion through treatment with weak acids or bases, as will be shown in the next lecture. Of special importance are the peptization phenomena in which an increased dispersion is brought about in a gel through the addition of traces of electrolytes. Freshly precipitated sulphids may thus be brought back into colloid solution by being treated with dilute hydrogen sulphid.

Let me illustrate peptization to you by an experiment devised by A. Lottermoser (demonstration). These five flasks all contain the same amount of freshly precipitated silver iodid. To one has been added water only. The remaining four contain equal amounts of differently concentrated potassium iodid solutions. The concentration of the potassium iodid increases in the order in which I have arranged these flasks, amounting in the last one to a one-fourth molar solution.[1] You observe how in the water and in the most concentrated potassium iodid solution the precipitate remains coarsely dispersed. The supernatant liquid in these is relatively clear. In the remaining flasks this liquid is of milky appearance, particularly marked in the middle one containing approximately a $\frac{3}{100}$ molar solution. In this concentration the gel has changed to a typical colloid solution of silver iodid.

Such dispersing effects due to low concentrations of

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[1] See A. Lottermoser, Koll.-Zeitschr., **2**, Supplement 1, 4 (1907); **3,** 31 (1908); **6,** 78 (1910); also, Zeitschr. f. physikal. Chemie, **62**, 359 (1908).

electrolytes are frequently observed, the ions capable of producing them being known as *stabilizing*, or *sol-forming* ones. Their effect is observable only when the gel is freshly precipitated and is possessed of a definite "mechanical" constitution. By the latter is meant that, in the fresh gel, the colloid particles are merely agglutinated and have not yet coalesced. Under such circumstances the ions can apparently give the "primary" gel particles an electrical charge leading to their electrostatic repulsion which in turn leads to the re-solution of the gel.

In many cases, both in emulsoids and in suspensoids, mere restitution of the original conditions suffices to make a precipitated colloid go back into solution. We say then that the colloid change is *reversible*. Generally speaking, reversible coagulations are commoner among the emulsoids than among the suspensoids. Still it is wrong to consider irreversibility of precipitation as directly characteristic of the coagulation of suspensoids, as is still done. Colloid silver, for example, yields a coagulum upon the addition of ammonium citrate or ammonium nitrate which is entirely reversible.[1]

§20.

In concluding this lecture, let us consider briefly that group of colloid changes in state which are comprised under the heading of *adsorption*. In keeping with what was said at the beginning of this lecture, we may regard adsorption as *that change in concentration which colloids and other dispersed systems suffer at the surfaces where they come in contact with other bodies*. This change in concentration is the only constantly observed behavior that is common to all the myriad manifestations generally grouped under the term *adsorption*. We shall, therefore, consider only this phase of the problem. *After* such a concentration difference has come to pass, a long series of secondary changes may take place.

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[1] See S. Odén and E. Ohlon, Zeitschr. f. physikal. Chemie, **82,** 78 (1913).

In cases of *positive* adsorption there commonly occurs a *fixation* of the colloid or of the dispersed material upon the solid, liquid or gaseous adsorbing surface. Under such circumstances, the rest of the dispersed system may be poured off without carrying away with it the dispersed material that has collected in the surface. Such fixation in the surface may be brought about, for instance, by the colloid being coagulated into a coherent layer. As a matter of fact, the mechanical coagulations discussed above rest in part upon such primary adsorption effects. The increase in concentration may go so far that the adsorbed material separates out in solid or even in crystalline form upon the edge of the adsorbent, as observable in the adsorption of organic dyes by charcoal. At other times the adsorbed material may wander into the adsorbent and there form a *liquid or solid solution.* This can occur of course only when the adsorbed materials are capable of diffusion, in other words, are molecular dispersoids. The phenomenon is illustrated by the adsorption of iodin by charcoal. Finally, in consequence of an accumulation of the dispersed particles in a surface, *chemical reactions* of various kinds, more especially polymerizations, may occur. Such are actually observed, for example, in the adsorption of amylenes.[1] More pronounced chemical reactions like hydrolyses, oxidations, etc., may also be observed. But all these changes are secondary and may be of totally different types in the different special cases of adsorption studied. The primary and only constant change which characterizes adsorption is found in the change in concentration of the dispersed material that occurs in the surface layer.

Before showing some adsorption experiments, it is important to emphasize that the intensity of adsorption is chiefly dependent upon the size of the adsorbing surface. It is for this reason that for practical adsorption purposes we use highly dispersed powders of carbon, fuller's earth, etc. The enormity of the adsorbing surfaces in such dis-

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[1] See L. Gurwitsch, Koll.-Zeitschr., **11,** 17 (1912).

persed systems is not generally appreciated, nor how greatly these grow with increase in the division of the particles. To illustrate the matter I append the following table which shows the surface increase of one cubic centimeter when undergoing decimal division:

INCREASE IN SURFACE OF A CUBE WHEN DECIMALLY DIVIDED.

Length of Cube Edge.	Number of Cubes.	Total Surface.
1 cm.	1	6 sq. cm.
1 mm.	10^3	60 “
0.1 mm.	10^6	600 “
0.01 mm.	10^9	6,000 “
1 μ	10^{12}	6 sq. m.
0.1 μ	10^{15}	60 “
0.01 μ	10^{18}	600 “
1 μμ	10^{21}	6,000 “
0.1 μμ	10^{24}	60,000 “
0.01 μμ	10^{27}	600,000 “
0.001 μμ	10^{30}	6 sq. km.

In this table is shown how a solid one centimeter cube of carbon acquires a total surface of 60 square meters when divided to the point of microscopic visibility (0.1 μ), and one of 60 to 600 square meters if the subdivision is carried through the colloid realm. A sugar manufacturer buying a cubic meter of charcoal for clarifying purposes receives when this consists of particles one millimeter in diameter, some 600 square meters of surface; while if the particles are 1 μ in diameter he receives six *million* square meters, or six square *kilometers* of adsorbing surface for his money. These figures illustrate to what extraordinary values these surface increases mount when dealing with highly dispersed adsorbents.

I want now to show you the wide distribution of these adsorption phenomena (demonstration). I have here a number of flasks filled with differently colored colloid and molecularly dispersed liquids: iron chlorid, fuchsin, berlin blue, congo red, colloid silver, colloid gold and colloid graphite. Standing opposite is an equal number of flasks, each containing a spoonful or two of bone charcoal (bone black). I pour upon the bone black in each of the flasks the contents of the flask opposite it and for a moment shake every mixture vigorously. I next pour all the mixtures, along with their bone black, one after the other into this large filter-lined funnel. In spite of the fact that I have carried out this whole procedure as rapidly as possible, you see that the filtrate runs through entirely clear. Adsorption has, in other words, occurred with extraordinary rapidity in all these cases and is *practically complete.*

To demonstrate that not only colored dispersoids and not only charcoal show such prompt adsorptive effects, I show you an experiment with a colorless alkaloid, quinin bisulphate, and a special preparation of fuller's earth, prepared by John Uri Lloyd of Cincinnati;[1] 10 cc. of the clear quinin solution are poured upon a half gram of the dry adsorbent, the flask is shaken and the mixture allowed to stand a moment. To prove to you that the original quinin solution was rich in this alkaloid — it was a 2.5 percent solution — I acidify it slightly and add Mayer's alkaloid reagent to it (demonstration). A heavy white precipitate forms at once. Let me now filter the adsorption mixture and repeat this test with the filtrate. One hardly expects, of course, that adsorption will be complete and that our filtrate will not show some slight turbidness, and yet as I perform the test you observe that the filtrate remains absolutely clear no matter how much reagent or acid I add.[2]

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[1] I am much indebted to Professor J. U. Lloyd for giving me the material necessary for this demonstration. The preparation appears in the trade under the name of Lloyd's Alkaloidal Reagent.

[2] According to the accompanying circular the following amounts of Lloyd's reagent are required. To adsorb completely one gram of cocainhydrochlorid, there are required of the reagent 10 grams; for one gram of strychnin sulphate, 10 grams of the reagent; for one gram cinchonin sulphate, 10 grams; for one gram cinchonidin sulphate, 10 grams; for one gram quinin bisulphate, 8 grams; for one gram atropin sulphate, 8 grams; for one gram brucin sulphate, 5.6 grams; for one gram codein sulphate,

When specific instances of adsorption are studied we observe considerable differences so far as intensity of adsorbing power is concerned. Acids, for example, are usually better adsorbed than their salts; and organic salts, better than inorganic. Substances of high molecular weight and colloids are especially well adsorbed. The ready adsorption of the latter has been regarded by many authors as specific of them. Of course there exist quantitative differences among these, too. If, in my previous experiment, I had chosen to mix a concentrated arsenious trisulphid with bone black and had poured this mixture upon the filter, I might not have been so successful in getting an absolutely clear filtrate.

Of much importance are certain quantitative relations as observed when adsorption is allowed to occur from solutions of different concentrations. Generally speaking, adsorbents take up *relatively* more from dilute solutions than from more concentrated ones. In most instances an adsorption maximum is attained beyond which no increased amounts of the adsorbed material are taken up by the surface of the adsorbent. The "concentration function"[1] of adsorption when graphically expressed has, therefore, a hyperbolic form as shown in Fig. 41, *A*. This concentration function of adsorption differs markedly from the concentration function expressing the

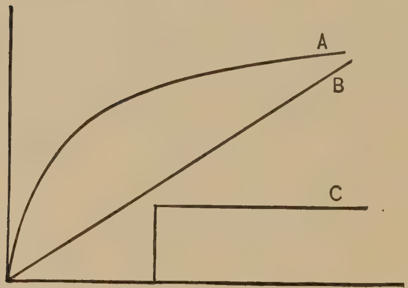

FIG. 41. — Diagram illustrating the concentration function in adsorption, in solution and in chemical combination.

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5 grams; for one gram morphin sulphate, 4 grams. The mixtures are usually prepared in from 100 to 200 cc. of water.

[1] In modern literature we frequently encounter the term adsorption isotherm as a designation for this concentration function. The use of this term represents a by no means justified coquetry with the simpler systems of physical chemistry containing but three variables (as is the case, for

distribution of a dissolved substance between two nonmiscible liquids. The distribution of a salt, for instance, between water and chloroform is represented by a straight line as shown by *B* in Fig. 40. For purposes of comparison, we may introduce the effects of the formation of stoichiometrical combinations of a *chemical* nature between adsorbent and adsorbed material. The two molecules reacting with each other might under these circumstances be regarded as adsorbent and material to be adsorbed, the adsorbed amount being calculated as number of molecules bound. Saturation of *all* the molecules considered as adsorbent by the material to be adsorbed would under such circumstances not be attained until a definite stoichiometrical concentration of the latter had been reached. At this point the number of the molecules constituting the adsorbent would be just enough to yield a definite chemical compound. But at this concentration all the molecules of the material to be adsorbed would have been used up and the composition of the reaction product would then not change even when an excess of the molecules being adsorbed was added. The whole process represented graphically would yield therefore a right angled curve, as shown in *C* of Fig. 41. All possible transitional types are discoverable between these three curves. Some of them are extremely interesting but their detailed consideration would lead us too far afield.

§21.

If it is asked what forces bring about these concentration changes in surfaces, it can only be answered that *a whole series of different kinds of energy* plays a rôle. That which

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example, in gases) in which, through exclusion of the one variable, the function of the remaining two is then easily obtainable. But in adsorption equilibria this does not hold true, since at constant temperature one may, for example, obtain a whole series of adsorption isotherms, dependent upon variations in the amount of absorbing material or variations in its specific surface. To speak of an "isotherm" under such circumstances is to invite objection. The expression "concentration function" is much to be preferred.

is common to all the forces active in adsorption is expressed in a generalization of Willard Gibbs' theorem, and reads as follows: *adsorption will take place whenever there exists in a surface a difference in energy potential which can be decreased through a change in the concentration of the dispersed materials bordering upon this surface.*[1]

To get a picture of what this means, imagine a solid dipping into a liquid toward which the solid possesses an electrical charge. There exists in the surface, in this case, an *electrical* difference in potential. If a dispersed phase carrying a charge opposite to that possessed by the solid body is present in the liquid, the difference in electrical potential can evidently be decreased by having the dispersed particles aggregate in the surface and so partially neutralize it. The consequence would be an electrical adsorption effect.

Next imagine two substances, such as two non-miscible liquids, between which there plays the ordinary surface tension. If the one liquid is a dispersoid whose surface tension against the second liquid *decreases* with increase in concentration, there will also be a tendency toward positive adsorption, the adsorption being this time *mechanical* in nature. This type of adsorption consequent upon decreases in surface tension was recognized by Willard Gibbs and J. J. Thomson, and has in recent years been the subject of much study. Its importance seems actually to have been overestimated, in that many writers have regarded it to be the only possible, or at least the only universally important, factor in all adsorptions.

Imagine, finally, that there exists between two phases, as between an adsorbent and a dispersoid, a *chemical* difference in potential. A chemical reaction is proceeding in the surface which, like most chemical reactions, increases in rate with increase in the concentration of the substances concerned in the reaction. Under such circumstances there

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[1] This extension of Gibb's rule was made in my Grundriss der Kolloidchemie, 1. Aufl., 434, Dresden, 1909.

would also appear a tendency of the dispersed phase to accumulate in the surface, thus yielding an adsorption in which the driving force would be *chemical* in nature.

Similar reasoning governs the effects of thermic and photic differences in potential in surfaces. A whole series of different energies, in other words, plays a rôle in adsorption, and these not only may be coördinated with each other, but may actually at times antagonize each other.[1] These facts will suffice to emphasize the importance of distinguishing in any individual case between the different kinds of energy that may be playing a part in the production of the adsorption.

§22.

Permit me, in conclusion, to touch upon the remarkable and interesting illustrations of adsorption that are seen in the *mutual adsorption of two colloids* or in the mutual adsorption of a molecular dispersoid and a colloid. Which in either illustration is the adsorbent and which the adsorbed material? Obviously in mutual adsorptions of highly dispersed systems all differences between adsorbent and adsorbed material disappear, just as in the union of two molecules with each other chemically. But this analogy to the "purely chemical" reaction goes further. In the mutual adsorption of two dispersed phases, the first change that occurs consists in a *decrease* in the degree of dispersion of the whole system. This is illustrated in the mutual precipitation of two oppositely charged colloids. But this is like the formation of a precipitate in any chemical reaction for which there is also necessary as a first change the mutual adsorption of two dispersed systems. Further, experiment has shown that the precipitation of colloids often necessitates the existence of the reacting

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[1] Such antagonistic and complex adsorption processes occur, for example, when electrical and surface-tension differences appear simultaneously in surfaces. See my Grundriss der Kolloidchemie, 1. Aufl., 435, Dresden, 1909.

materials in *definite* concentrations.[1] The quantitative relationships obtaining in the reaction mixture may actually yield stoichiometrical values.[2] These facts further demonstrate the analogy between adsorption and the chemical union of molecules and show how difficult it may be under some circumstances to determine whether the formation of a precipitate has been occasioned by purely chemical means or by those associated with the physical consequences of adsorption. Finally, if it is recalled that adsorption phenomena are known which are dependent upon certain chemical relationships, we become aware of the bridge which exists between colloid-chemical reactions and the purely chemical ones. The relationship between the two appears to be so close that its consequences, when applied to our present "chemical" notions, seem nothing short of startling.

§23.

I cannot say that with these remarks and with these experiments on theoretical colloid chemistry, I have concluded the subject, though necessity compels me to break off here. I can only hope to have made you realize the wealth of material that this new science possesses. Had I had at my disposal twice the time allotted me, I could still only have given you a sketch of the field. In the two lectures that follow I shall try to give you a glimpse of the scientific and technical applications that may be made of colloid chemistry.

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[1] See especially the papers of J. M. van Bemmelen, W. Biltz, etc. References may be found in my Grundriss der Kolloidchemie, 1. Aufl., 404, Dresden, 1909.

[2] See, for example, A. Sanin, Koll.-Zeitschr., **13,** 305 (1913).

IV.

SOME SCIENTIFIC APPLICATIONS OF COLLOID CHEMISTRY.

FOURTH LECTURE.

SOME SCIENTIFIC APPLICATIONS OF COLLOID CHEMISTRY.

We shall devote these last two lectures to the applications that may be made of colloid chemistry. Applications may be made of a science under two headings. One science may be applied to a second, for example. Not only is this possible but it must be done in certain instances as when the principles of physics or of chemistry are applied to biology or mineralogy. We cannot, of course, apply haphazard any given science to some other. While chemistry, for example, may be applied to the biological problem of heredity, the converse cannot be done, though into the philosophical reasons for this we cannot enter here.[1] Second, we may apply science to technical, practical and industrial problems.

Colloid chemistry also finds application in these two ways. In fact I cannot begin a discussion of this question without declaring that *since the birth of the so-called classical physical chemistry of the molecular solutions, some thirty-five years ago, no branch of physics or chemistry has arisen which can be compared in importance, so far as scientific and technical applications are concerned, with that of colloid chemistry.* I am fully aware of the magnitude of this claim, yet, as this and the next lecture will show, I stand ready to defend this thesis. I know very well, for example, that radio-chemistry, which in point of age may be regarded as a sister science to colloid chemistry, has yielded results which have modified most drastically and broadened in surprising fashion our concept of nature; but so far as the applications are concerned that may be made of it, either in point of number or

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[1] The application of one science to another is regulated by the relations expressed in the well-known pyramid of the sciences of A. Comte and Wilhelm Ostwald.

in variety, to scientific and technical problems, even radiochemistry cannot compare with colloid chemistry.

§1.

If I have previously complained that the wealth of phenomena and ideas embraced in pure colloid chemistry was too great to permit me to give you a proper conception of it, I can only complain more loudly when I am asked to outline the applications that may be made of this science. I do not believe that anyone would even today essay to read all the papers that have been written, for example, on the applications of colloid chemistry to biological and medical problems. Whole books are required to give you the colloid-chemical views that are of such paramount importance in even such special and technical fields as those of dyeing and tanning. It is no exaggeration to say that no week has gone by in the past ten years (and of course does not go by today) in which a new body of scientific or technical facts is not recognized as essentially colloid-chemical in nature, and in which it is not shown how the application of colloid chemistry to such phenomena not only brings immediate light but promise of even more in the future. In such development over-enthusiasm of course will sometimes evidence itself and then problems will be designated as colloid-chemical which in reality belong in a different category of science. But in spite of such occasional lapses, everyone who knows the history of applied colloid chemistry will agree not only in admitting that the number and the variety of the problems to which colloid chemistry is applicable is already amazingly large, but that the ultimately attainable by such application can at present hardly be imagined. Speculation in colloid-chemical futures is still entirely safe.

In discussing with you the applications of colloid chemistry I must, because of limited time, take my choice between presenting a few illustrations in some detail, or a larger number more superficially. I shall follow the second course which, though less satisfactory in some respects, will best serve to emphasize for you the varieties of colloid-chemical application.

§2.

When we take up the scientific applications of colloid chemistry, we recognize at once that a great number of such may be made within the field of chemistry itself. We need but recall our first lecture to recognize how a discussion of *precipitates* and of their properties of passing through filter paper at once plunges us into the midst of that branch of chemistry in which we received our first instruction, namely, *analytical chemistry.* The rules laid down by analytical chemistry with an eye to avoiding the "going through" of a precipitate, such as the working with relatively concentrated solutions, the setting aside of the precipitate, moderate heating, the addition of salts, etc., are all of them methods, as you see, of utilizing the influences of concentration, of ageing, of coagulation and of the effects of salts in determining the degree of dispersion of colloids and their precipitation.

Another interesting application of colloid to analytical chemistry is seen in the methods employed for *recognizing traces of the noble metals.* In discussing the colors of colloids, I called your attention to the great intensity of those shown by the noble metals when these are colloidally dispersed. At times it may even exceed that of the aniline dyes. It is natural that this property of the noble metals should have been called upon for analytical purposes, and so it does not surprise us that one of the oldest and best known methods of demonstrating the presence of traces of gold consists in reducing this to colloid form. The *Cassius purple test for gold* is a typical illustration of the production of gold in colloid form and its subsequent precipitation in the form of an adsorption compound through a second colloid. The first step in the test is accomplished through the reduction of the gold salt by stannous chlorid. In this way colloid gold and colloid stannous acid are produced, which then unite to form the well-known, reddish-violet precipitate.

We are familiar with still more sensitive colloid-chemical methods of demonstrating minute traces of the noble metals of which I should like to show you one (demonstration). As shown by the far too little known and appreciated investigations of J. DONAU, dilute solutions of the noble metals are reduced in our common borax beads to solid colloid solutions. In this way different colors are imparted to the otherwise colorless bead, which differ with the character of the metal and its degree of dispersion. Let me fill this platinum loop with some powdered borax and then heat it in a Bunsen flame. When the salt begins to "foam," I moisten it carefully with a very dilute solution of gold chlorid and then, by further application of heat, melt the whole mixture to a bead. As you observe, the bead assumes the rose color familiar to you as characteristic of highly dispersed gold. Were I to use a more concentrated gold chlorid I should obtain a violet or blue bead. These correspond, as you know, with less highly dispersed grades of reduced gold. Even the red bead will, with prolonged heating, usually turn violet, for under such circumstances the dispersion value of the gold is progressively decreased until coagulation occurs.

With silver salts one can obtain blue or yellow beads; while platinum salts yield violet ones. The great sensitiveness of these color reactions is of much interest. Spectrum analysis is, as you know, generally recognized as of extreme delicacy, and yet, so far as the demonstration of the presence of the noble metals is concerned, these colloid methods may not only equal spectro-analytic ones, but in certain cases even exceed them in sensitiveness. The smallest amount of gold that may be recognized spectroscopically is $\frac{130}{1000000}$ of a milligram. $\frac{2}{1000000}$ of a milligram may be recognized by colloid-chemical means. $\frac{130}{1000000}$ of a milligram of platinum may be recognized spectroscopically, while $\frac{50}{1000000}$ suffice for its recognition colloid-chemically. Spectrum analysis is more sensitive than the colloid-chemical in the case of silver, $\frac{50}{1000000}$ of a milligram of silver being recognizable by the first method against $\frac{180}{1000000}$ by the second.[1]

In the experiments on the production of colloid gold, I emphasized the very different substances that may be used as reducing agents. Certain of the organic reducing substances act peculiarly energetically in this regard. It is for this reason that the formation of colloid gold may be used for demonstrating the presence of *organic reducing materials*. The so-called *humic acids*, for example, which give our soils their black color, and which are usually found in the soil in colloid form, reduce gold solutions to colloid gold in such low concentrations that this reaction has long been used to prove their presence.[2]

The principle is used in similar fashion in Ley's test for the distinction of natural from artificial honey. In this, an ammoniacal silver nitrate solution is reduced by the addition of a few drops of very dilute honey. The metallic silver that is produced assumes the reddish-yellow color of the colloid metal, when natural honey is used, while a darker, more greenish, precipitate is formed by artificial honey. Traces of albumin or of ethereal oils present in the natural product are probably responsible for the difference. Their "protective action" serves to maintain the colloid silver in a higher degree of dispersion in the natural product than in the artificial one. While I would not recommend such an attempt, it should not be a difficult thing for a colloid chemist to do away with this difference between the naturally and the artificially produced honey by discovering a material which when added to the latter would take the place of the natural protective colloid. The practical result of such an investigation would probably then bring about a reversal in the application of Ley's test, for the manufacturers would in this case, as usually, add too much of the substance.

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[1] See J. Donau, Koll.-Zeitschr., **2**, 273 (1908).

[2] See P. Ehrenberg, Koll.-Zeitschr., **5**, 30 (1909).

§3.

Let me touch next upon some applications of colloid chemistry to inorganic and *photo-chemistry.* A much discussed and most fascinating problem in this field concerns the chemical nature of the substances comprising the *latent picture.* It is a well-known fact that this depends upon the presence of certain reduction products of silver haloids; in other words, upon the presence of compounds which contain more silver and less halogen than is represented, for instance, by the formula AgCl. These reduction products of "photo-haloids" are, moreover, differently colored (yellow, red, violet, blue, etc.). Until recently it was thought that they all consisted of "sub-haloids," compounds having some such formula as Ag_2Cl. The drawbacks to this view reside in the fact that such sub-haloids have never been isolated; that one is compelled to hold to the existence of a whole series of them (as α, β, γ, δ, etc., haloids) having different colors; and that they must be assumed to be able to pass easily from one form to another. You will perhaps at this point recall the different colors that colloid silver assumes and so yourselves reach a conclusion which has been well developed by LÜPPO-CRAMER[1] in his numerous and careful studies of the subject. The photo-haloids are not chemical compounds containing silver and halogen in stoichiometrical proportions, but represent *adsorption complexes of colloid silver in different degrees of dispersion with normal, non-reduced silver haloids.*

The correctness of this view has been demonstrated by the experiments of W. REINDERS,[2] who has succeeded in producing these photo-haloids synthetically in the form of differently colored crystals by allowing different silver haloids to crystallize in the presence of differently colored

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[1] See the numerous papers of LÜPPO-CRAMER dealing with the relations of colloid chemistry to photography throughout the volumes of the Kolloid-Zeitschrift. See also his books, Kolloidchemie und Photographie, Dresden, 1908, and Kolloides Silber und die Photohaloide, Dresden, 1908.

[2] See W. REINDERS, Koll. Zeitschr., **9**, 10 (1911) where references to the literature may be found.

colloid silvers. The crystals took up the colloid silver and ultimately appeared with its color. This is certainly beautiful proof.

In passing, I should like to point out that numerous other colloids, as the organic dyes, may be thus taken up by crystals. Gelatin may also be absorbed. These facts deserve much consideration, for they show that the process of crystallization in the presence of a colloid does not always represent a purification of the crystallizing material. Other illustrations might be introduced to show how crystals may take up colloids as impurities. In fact, such complexes have led to erroneous conclusions regarding the existence of different chemical compounds, as in the case of the so-called chromisomers, when really none such existed.[1]

Time permits me only to mention the fact that many allegedly chemical compounds have proved to be colloid in nature. Many of the *hydrates*, for example, are now known to be colloid or adsorption compounds, as illustrated in the different silicic acids which hold water.[2] On the other hand, compounds like the allegedly different stannic acids have turned out to be one and the same substance existent in different degrees of dispersion,[3] and the so-called "solutions" of the alkali metals and of silver in liquid ammonia are probably of colloid nature.[4]

§4.

The applications of colloid chemistry to *organic chemistry* are not only already very extensive, but promise to multiply.

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[1] Such a fictitious color isomerism was discovered, for example, by O. Hauser, Ber. d. Dtsch. Chem. Ges., **45**, 3516 (1912), in the case of potassium ferrocyanid, in which through the presence of colloid berlin blue a fictitious color isomerism was brought about. I believe that many other alleged examples of color isomerism depend upon just such colloid-chemical phenomena.

[2] See the numerous papers of J. M. van Bemmelen in Die Absorption, edited by Wolfgang Ostwald, Dresden, 1910.

[3] See W. Mecklenburg, Zeitschr. f. anorganische Chemie., **64**, 368 (1909); **74**, 207 (1912); a review is found in Koll.-Zeitschr., **11**, 202 (1912).

[4] See Wolfgang Ostwald, Kolloidchem. Beihefte, **2**, 437 (1908).

All those sticky, mucilaginous, resinous, tarry masses which refuse to crystallize, and which are the abomination of the normal organic chemist; those substances which he carefully sets toward the back of his cupboard and marks "not fit for further use," just these are the substances which are the delight of the colloid chemist. For in most instances these properties are the properties of colloids, more particularly of that group of them known as the solvated emulsoids.

Among the solvated colloids appears a class which we have not discussed as yet, namely, that of the *isocolloids*.[1] Please recall that by the term *colloid* we mean nothing more than a dispersoid in which the degree of dispersion has a definite value. Now we cannot only conceive of, but we actually know of, instances in which the dispersed phase and the dispersion medium have the same chemical composition and yet the two do not form a homogeneous or molecularly dispersed system. Thus, a polymeric compound is very frequently not molecularly soluble in its monomeric form, and this is true for many pairs of chemical isomers. To illustrate the fact in entirely modern fashion, we need but consider the artificial synthesis of rubber through polymerization of isopren. Through prolonged heating, the isopren is polymerized to a colloid product, which at first dissolves colloidally in the monomeric isopren, greatly increasing its viscosity.

Isocolloids may be produced from a single chemical element, for, as you know, certain elements may exist in different so-called allotropic states. These may then be divided colloidally into each other.[2] You are all well aware

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[1] The concept of the isocolloid was first set up and developed by me in my Grundriss der Kolloidchemie, 2. Aufl., 128, Dresden, 1911.

[2] The objection of many phase rule theorists that because of the laws of equilibrium isodispersoids *cannot* exist, looks to me like an attempt to do violence to nature. These things do exist, as plainly evidenced by the numerous mixtures which consist of nothing but one element into which that same element has been dispersed in allotropic form. See my Grundriss der Kolloidchemie, 2. Aufl., 128, Dresden, 1911. To the examples given there might be added other metals, as tin and zinc. Just because these

that silver or phosphorus, for example, may appear in a whole series of different physical states or allotropic forms. In keeping herewith, we know of a whole series of mixtures of such allotropic modifications which have been proved, or may be proved, to be colloid mixtures. White phosphorus, on exposure to light, gradually changes to the red form. When this change is studied ultramicroscopically, the allotropic transformation may be observed directly. Under the influence of the light, particles of colloid dimensions are produced, which gradually coalesce to form larger aggregates with a net or honeycomb structure.[1] In silver melts at temperatures between 160 and 200° C., we probably also deal with colloid emulsoids consisting of two forms of silver. This is rendered probable by the fact that the viscosity changes observed in this temperature realm are identical with those observable in typical colloid mixtures.[2] To these isodispersoids, more particularly the isocolloids, belong also the various resins, many oils and probably the majority of those troublesome organic residues which fail to crystallize.

But illuminating results will also follow the application of colloid chemistry to other branches of organic chemistry, as to that of the *dyestuffs*. They are certainly to be expected, for a large number of the organic dyestuffs form typical colloid solutions in water. Since the properties of such solutions depend upon the degree of dispersion, it is to be expected that changes in this colloid state of the dyestuffs cannot fail to be of importance in the dyeing properties of the dyes themselves. Colloid chemistry has already been asked to shed light upon certain dyestuff problems, where attempts to explain the phenomena observed through the

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systems do not fit into theories of equilibrium, they do not therefore disappear from nature, nor do they lose in this fashion their great scientific and practical significance.

[1] See H. Siedentopf, Ber. d. Dtsch. Chem. Ges., **43**, 692 (1910).

[2] See Wolfgang Ostwald, Grundriss der Kolloidchemie, 2. Aufl., 131, Dresden, 1911; or Handbook of Colloid Chemistry, Trans. by Fischer, Oesper and Berman, Philadelphia, 1915. See also Koll.-Zeitschr., **12**, 220 (1913).

orthodox ones of chemical constitution have given only arbitrary explanations or failed entirely. It has been found that a large number of the colloid organic dyestuffs behave as do the colloid metals. They change their color, for instance, with the degree of their dispersion, passing from yellow through red to blue just as do colloid gold or silver.[1] Red colloid gold, for example, becomes blue upon the addition of an electrolyte but *at the same time* coarser.

Perhaps you know that the color changes of *indicators*, like congo red, are also accompanied by variations in degree of dispersion. They used to be attributed to purely chemical changes. When an acid was added to congo red, for example, it was held that the insoluble dye-acid was freed. That such a purely chemical explanation is not always adequate may be demonstrated with an indicator closely allied to congo red, namely, congorubin (demonstration). Congorubin changes color not only upon the addition of an acid or upon the addition of larger amounts of alkali but, what is most important, when all manner of neutral salts are added, as sodium chlorid or magnesium sulphate (demonstration). The addition of a neutral salt brings about the change in color even in the presence of free alkali, for example in 1/10 normal sodium hydroxid. Barium hydroxid and sodium hydroxid for example, change congorubin to blue at once (demonstration). There occurs in all these cases, as the color changes to violet or blue, a decrease in the degree of dispersion of the congorubin as may be proved by ultra-filtration, by ultra-microscopic observation or, at times, direct observation with the naked eye. The formation of a free dye-acid is out of the question in the presence of so much free alkali. These experiments and others of similar type indicate clearly, therefore, that changes in the degree of dispersion of the dye are to be held responsible

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[1] See Kolloidchem. Beihefte, **2,** 409 (1911); Koll.-Zeitschr., **10,** 97, 132 (1912).

for the changes in color just *as when a gold sol changes from red to blue.*[1]

§5.

Colloid chemistry finds many applications, too, in the realm of its sister science, *physical chemistry*. There exists the closest possible relation between colloid chemistry and capillary chemistry. Colloid chemistry is in reality nothing but a special division of capillary chemistry, for both deal chiefly with systems which consist essentially of surface. On the one hand, the phenomena of surface tension, of adsorption and of capillary electricity find immediate application to colloid chemistry, while this sheds new light into the field of capillary electricity.

But there also exist relationships between colloid chemistry and more distant realms of physical chemistry. As you know, the classical solution laws of VAN'T HOFF and others begin to show exceptions when concentrated solutions are studied. Now call to mind, in this connection, what has previously been emphasized, that these concentrated solutions often exhibit the earmarks of the colloid state by showing the TYNDALL phenomenon, by becoming viscid, etc. It has been suggested recently, especially through the work of American investigators, that in these concentrated molecular solutions there occurs a fusing of the dissolved particles with the solvent — in other words, *solvation*. It is assumed that the ions or molecules of the dissolved substance unite, under certain circumstances, with a large number, one hundred or more, of the molecules of the dispersion medium. No one seems thus far to have even

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[1] For an exhaustive monograph on the changes in color of congorubin considered from a colloid-chemical point of view see WOLFGANG OSTWALD, Kolloidchem. Beihefte, **10,** 179 (1919); also **11,** 74 (1919); **12,** 92 (1919); Koll.-Zeitschr., **24,** 67 (1919). See also the several studies of H. LÜERS, R. HALLER, R. KELLER, etc., in the more recent and current volumes of the Kolloid-Zeitschrift.

hinted that whenever a thousand molecules unite in this fashion, complexes of colloid dimensions must result as a matter of necessity. In such solvates the amount of the dispersion medium bound by the molecules varies progressively and cannot therefore be expressed through simple stoichiometrical relations. Careful study of the problem shows that between the laws governing such solvation, and those which govern the formation of adsorption compounds[1] there exists a whole series of analogies. As previously noted, solvation is characteristic of a large number of colloids. A particle of albumin or gelatin, for example, readily holds a thousand times its own weight of water.

These considerations must render it apparent that we are destined to discover solution laws which will embrace both these classes of dispersoids. The coarse colloids (perhaps even the coarse dispersions) will occupy one of the extremes under these laws, the dilute molecular dispersoids the other. At the present moment these laws are known only in their beginnings or are still undiscovered,[2] but I believe that the view here expressed will bear better fruit than the attempt, constantly made now, to make adequate the laws governing dilute solutions by everchanging additions and corrections. Since the behavior of the molecular dispersoids passes gradually over into that of the colloid systems, such more general laws as are here discussed would naturally embody from the beginning the corrections which need constantly to be made in laws governing dilute solutions when the attempt is made to make these cover the anomalous behavior of the concentrated molecular solutions.

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[1] See Koll.-Zeitschr., **9,** 189 (1911); see also the paper of Wolfgang Ostwald and K. Mündler, Koll.-Zeitschr., **24,** 11 (1919) in which is shown that the solvation or swelling of solid gels like rubber or gelatin is governed quantitatively by the same equation as the "osmotic" absorption of water by cane sugar solutions, etc.

[2] See the preceding footnote.

§6.

It is not a mere accident that the three most modern branches of physical chemistry — those of *catalysis*, of the *crystalline liquids* and of the *radio-active substances* — show interesting relationships to colloid chemistry. So far as catalysis is concerned — the science of the changes in the rate of a reaction through the presence of an added substance which does not appear in the products of that reaction — I pointed out in the second lecture that colloids are peculiarly active as catalyzers. But not only do colloids themselves bring about such catalytic effects, but other materials rich in surface, even though not colloidally dispersed, act in similar fashion. I need but point out the contact effects exhibited by platinum black and other metallic powders in the production of sulphuric acid; and the use of finely powdered metallic hydroxids, etc., in various catalyses as developed by J. Sabatier. It has also been discovered that the effect of the walls of the containing vessels, as in various gas reactions, is in large measure dependent upon their roughness.

If we try to say how the element of surface favors such "heterogeneous catalyses," the effects of adsorption at once come to mind. Adsorption, as previously emphasized, depends not only upon the absolute but upon the specific surface (the quotient of surface divided by volume or weight). Therefore when the absolute or relative surface in a reaction system is increased, it means increased adsorption, and such increased adsorption means increase in the concentration of the reacting materials. This process may be further aided through the local production of heat which so frequently accompanies adsorption. The two processes together will serve to explain a large part of the increase in reaction rate seen in these systems. Secondary chemical reactions may also be made responsible for a group of these catalytic effects. Such secondary chemical reactions are also rendered possible through adsorption effects. As previously explained, the great or specific adsorption of one of the constituents of a reaction mixture may change the whole system of chemical equilibrium in that mixture. These facts will suffice to show why it is a matter of paramount importance that the ferments of the living organism are for the most part colloid in nature and why a study of their reactions from the point of view of colloid chemistry and of adsorption catalysis promises so very much.

A second subject in physical chemistry to which colloid chemistry finds application concerns the liquid crystals, or, as they are better called, the crystalline liquids, those peculiar substances whose refraction behavior relates them closely to the solid crystals. Those of you who are interested in these substances will know that a question concerning them has long been discussed, which, in startling fashion, is practically identical with that which is constantly raised in the problems of colloid chemistry. The question at stake is whether the crystalline liquids, which at times are distinctly turbid or refractively colored[1] and often highly viscid, are homogeneous or molecularly dispersed systems, or whether they are heterogeneous systems of the type of the emulsions. As in the case of the colloids, many facts seemed to argue for the first of these conceptions and many for the second. But just as with the colloids, discussion of this problem has, strictly speaking, brought no decision either way. The most widely accepted theory of the classical physical chemists is that of N. Bose, which holds that swarms of molecules, in other words, loose combinations of a number of molecules, swim about in the crystalline liquid. But this concept of a "swarm of molecules" is evidently nothing more than the designation of submolecular or colloid aggregates; and even though this word "colloid" has entered into the discussion only recently,[2] more and more evidence is ac-

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[1] See the second footnote on page 61.

[2] See Koll.-Zeitschr., **8**, 270 (1911).

cumulating to indicate that, at least in many instances, the *crystalline liquids are typical emulsion colloids.*[1]

Besides the fact that these liquids are turbid or opalescent, we need but emphasize their peculiar behavior regarding changes in viscosity when they are chilled. The viscosity curve again assumes a form identical with that observed when separation phenomena occur in critical fluids, as during the coagulation of albumin by heat, in the separation of sulphur melts,[2] etc.

That these crystalline liquids have a colloid degree of dispersion has also been proved directly, in many instances, by means of the ultramicroscope. Further evidence in this direction is offered by the changes in optical properties which these systems show upon the addition of small amounts of chemically indifferent substances. The close relation between the crystalline liquids and the colloid state is most strikingly illustrated perhaps in the behavior of an organic sulphonic acid recently studied by H. Sandqvist.[3] This substance in dilute solution in water behaves as a normal electrolyte but in more concentrated form the solution not only becomes colloid but shows, at the same time, the typical properties of a crystalline liquid. This classification of the crystalline liquids with the colloid dispersoids does not, of course, explain their optical peculiarities, but, by following a lead which concerns an almost forgotten microscopic phenomenon of capillarity, it is possible that light may be found.

Entirely normal, isotropic liquids, like water, show distinct polarization phenomena when they are observed in a dispersed state, in other words, in droplet form.[4] The

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[1] See especially the newer papers of The Svedberg, Koll.-Zeitschr., **16,** 103 (1915); **18,** 54, 101 (1916); **20,** 73; **21,** 19 (1917); **22,** 68 (1918).

[2] See Koll.-Zeitschr., **12,** 213 (1913).

[3] H. Sandqvist, Koll.-Zeitschr., **19,** 113 (1916).

[4] See V. von Ebner, Untersuchungen über der Anisotropie organisierter Substanzen, 2, Leipzig, 1882; O. Bütschli, Untersuchungen über Strukturen, 31, 35, Leipzig, 1898, where references may be found to earlier observations.

phenomenon has been designated surface polarization and has been attributed to the action of surface tension, which, in tiny droplets, comes to assume a considerable value. The amount of this surface polarization, on the one hand, increases with increasing degree of dispersion. On the other hand, its type, sign and value must be influenced by the chemical nature and perhaps the shape of the molecules. It may be — I make this suggestion with all reserve — that we will find here a bridge between the surface tension phenomena of microscopic droplets and the optical properties of systems, which like the colloids, consist almost entirely of surface.

The third modern — perchance most modern — branch of physical chemistry, into which colloid chemistry has recently penetrated, is that of *radio-chemistry.* Some years ago I suggested that it would be an especially interesting feat in synthetic colloid chemistry could the radioactive elements be obtained in colloid form.[1] Two years ago it was shown that nature has already made this experiment. *It was found that a whole series of aqueous solutions of radioactive substances are colloid in nature.*[2] These solutions show the phenomena of electrophoresis, of coagulation through electrolytes, they do not diffuse or dialyze, are easily adsorbed through other colloids, etc. Not all radioactive substances, but the majority, are found in this colloid state; hence colloid-chemical methods, as those of dialysis, absorption, etc., may be utilized to accomplish their separation and concentration. This is certainly a very startling and interesting application of colloid chemistry.

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[1] See my Grundriss der Kolloidchemie, 2. Aufl., 121, Dresden, 1911.

[2] See F. Paneth, Koll.-Zeitschr., **13,** 1, 297 (1913); T. Godlewski, Koll.-Zeitschr., **14,** 229 (1914) as well as the excellent review of this subject by F. Sekera, Koll.-Zeitschr., **27,** 145 (1920).

§7.

But observations upon dispersed (more particularly colloidally dispersed) systems have yielded valuable fruit in another field which interests chemists and physicists alike. I refer to the experimental determination of Avogadro's *constant*, the famous value N, which states how many molecules are contained in a gram-molecule of any substance. There exist different methods by which this fundamental figure may be determined, of which I shall mention only the following.

As you know, the atmosphere surrounding the earth becomes rarer as we ascend. The matter is expressed in the law that with arithmetic progression upwards, the density of the atmosphere decreases geometrically. In the kinetic theory of gases, this law may be used for determining the value of Avogadro's constant in that the degree of barometric change which follows the unit decrease in density is inversely proportional to the gram-molecule of the gas.[1] *According to* J. Perrin, *this same change in concentration under the influence of gravity is also shown by dispersoids, provided the particles are so small that they show* Brownian *movement.* The concentration of the dispersed substance in any mass of colloid material is, therefore, always greater at the bottom of a vessel than at its top. At a given height this difference is the greater, the coarser the dispersion. In suspensions of gutta-percha or mastic, in which the particles are about 0.3 μ in diameter, the concentration of the particles 50 μ above the bottom of the dish is only half that of the bottom, while in the case of the earth's atmosphere, the density does not fall to half that obtaining at the surface of the earth until a height of six kilometers is reached. But Perrin was able to show that the same law not only holds for the distribution of

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[1] For details see J. Perrin, Die Atome, Deutsch von. A. Lottermoser, 2. Aufl. Dresden, 1920.

gases and of the particles in coarser dispersoids, but that one can calculate the value of AVOGADRO'S constant, when it is assumed *that every dispersed particle behaves like a molecule.* A "gram-molecule" of the dispersed particles would, therefore, equal their weight times N. The values thus obtained are in striking accord with those found by other methods and yield a value of 6 to 7.10^{23} molecules in the gram-molecule.

I can only touch upon the fact that AVOGADRO'S constant can also be calculated from the velocity of Brownian movement and that when this is done the same value is obtained. It is certainly remarkable that from the observation of a single particle of oil or mercury — even from the study of a drop of diluted milk (DECKHUYZEN) — so fundamental a value as that of AVOGADRO'S constant may be calculated.

§8.

I beg you now to follow me to still greater heights. You may, perhaps, think that I am joking when I say that colloid chemistry has already found interesting applications in the realm of cosmic physics and that in the future it will find still greater ones. Consideration of our universe will at once reveal to you that in it we deal not only with bodies of great mass and with those of molecular dimensions, but that it also betrays the presence of dispersoids possessed of very different degrees of subdivision.

Of special interest are the dispersoids of the sky as observed in atmospheric dust and in the atmospheric water (steam, clouds, fog, rain and snow). I have already emphasized that the blue and yellowish-red colors of the heavens depend upon the dispersoid nature of the atmosphere, and that these color effects rest upon the same grounds as the opalescence of typical colloids. In both instances we deal with a selective diffraction by particles of a diameter less than the length of a light wave. The analogy between the opalescence of the heavens and that of a mastic solution is so great that the same formula governs both phenomena. Even the polarization effects observable in them are entirely similar in the two cases.[1]

I should like, in passing, to direct attention to yet another optical effect, in which the presence of tiny, light diffracting particles plays a great rôle, namely, that of ordinary daylight. If the light of the sun were not diffused through the dispersoids of the earth's atmosphere, there would be no daylight in the ordinary sense of the term. The sun, like the moon, would stand in the heavens as a bright, burning disc upon an entirely black background. Wherever the sunlight did not strike directly, there would exist deep shadow; there would exist everywhere a garish contrast between the lighted and the unlighted. In short, the world would look entirely different. We are indebted to the atmospheric dispersoids for our ordinary "daylight."

But clouds (which are, for the most part, dispersoids of the composition gas + liquid) also behave like colloid systems. It is difficult to determine accurately the size of the water droplets composing clouds, but we seem to deal with particles of approximately colloid dimensions. This is proved not only by the fact that they float in the air, but also by the degree of polarization shown by the light emanating from them. These heavenly dispersoids also show a "coagulation" which is typical of emulsoid systems. The product of this coagulation we call rain. All this is also not a joke. We even know which factors are chiefly concerned in producing the coagulation of these heavenly dispersoids. Electrical changes are most important in that these bring about a coalescence of the highly

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[1] See J. M. Pernter, Denkschr. Ak. d. Wiss. Wien, **73**, 301 (1901); as well as his Physikalische Meteorologie.

dispersed water particles and so lead to their "precipitation" in the true sense of this term.[1]

But the applications of colloid chemistry may mount still higher. I suspect that a large number of you have read SVANTE ARRHENIUS' interesting volume "Das Werden der Welten." If you have, you will recall that in the theories of this investigator regarding the origin of the earth, two factors play an especially great rôle, namely, light pressure and the presence of the universally distributed cosmic dust. In the movement of cosmic dust through light pressure ARRHENIUS sees one of the most important reasons for different cosmic phenomena. In the production of a new heavenly body a shifting and an accumulation of cosmic dust brought about through light pressure is assumed to play an important rôle. It is therefore of great interest that K. SCHWARZSCHILD and certain other physicists have calculated that the size of these cosmic particles is not without influence upon their velocity. Particles too small or too large are moved less easily than those of medium size and calculation yields an optimum for movement when they have a diameter of about 0.16 μ. But, as you will recall, this value places them in the realm of the colloids. The size of cosmic dust is therefore ideal for these cosmic displacements. This conclusion regarding the optical motility of particles of medium size under the influence of light pressure has recently been verified experimentally by F. EHRENHAFT. Colloid particles of a medium degree of dispersion show an optimal "photophoretic" velocity. The optimal radius of silver particles moving in the concentrated light cone from an arc lamp was found to be 0.09 to 0.098 μ, the absolute velocity being 180 μ/

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[1] After WOLFGANG OSTWALD [Koll.-Zeitschr., **1**, 333 (1907) and page 118 of the first (1915) German edition of this book] and P. PAWLOW [Koll.-Zeitschr., **8**, 18 (1911)] had called attention to the relationship existent between these "dispersoids of the heavens" and the dispersoids of the laboratory, A. SCHMAUSS [Zeitschr. f. angew. Chem., **32**, 811 (1919); Chem. Ztg., 884 (1919), etc.] took up the problem anew and developed it.

seconds.[1] The illustration again shows the relation between degree of dispersion and properties which attain a maximum in the colloid realm. That colloid chemistry should in this fashion be of importance in the production of new worlds, — more than this could hardly be asked of it.

§9.

We shall now leave these ethereal regions and glance in the opposite direction. Mineralogy, geology, soil chemistry, agricultural chemistry — these are the sciences in which colloid chemistry has found brilliant application. In fact, it has long been at home in these fields.

Under the heading of *mineralogy* we naturally deal chiefly with solid colloids. In order to give you at once a particularly pretty example, I present these specimens of blue rock salt. It was long debated to what this blue color is due, for chemical analysis revealed no constant differences between the ordinary colorless rock salt and this blue product. Organic impurities were often imagined to be responsible, while other authors held that, as in the "silver haloids," blue-colored sub-haloids of sodium were responsible. But recent experiments — more particularly ultramicroscopic and synthetic studies — have demonstrated that we have to deal with a colloid subdivision of metallic sodium in the solid NaCl. Ultramicroscopic examination shows blue rock salt to contain numerous intensely colored and fairly regularly arranged colloid particles which do not appear in the colorless mineral.

The blue rock salt can, moreover, be produced artificially, according to the experiments of H. Siedentopf, in the following manner. A piece of colorless rock salt and a piece of metallic sodium are together sealed in a glass tube; the tube is evacuated, and its contents then heated

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[1] F. Ehrenhaft, Physik. Zeitschr., **18**, 368 (1917).

to above the vaporization point of sodium. The rock salt now assumes a yellowish color which ultramicroscopic investigation shows to be due to a molecularly dispersed solution of the sodium metal in the rock salt. The yellow-colored preparation is then carefully heated a second time to definite temperatures, recooled and perhaps heated again. In this way there is obtained, first, a reddish-violet, and then a blue rock salt. This treatment of the yellow preparation brings about a condensation of the originally molecularly dispersed metal into larger particles which finally assume colloid dimensions. We deal, in other words, with a typical colloid-chemical condensation method.

Let me emphasize in passing that similar procedures — the production of a highly dispersed solution which through its cooling, reheating and subsequent recooling is made to yield a dispersoid of colloid dimensions — are used to produce gold ruby glass, ultramarine, certain forms of steel and many of the organic sulphur dyes. I must also mention that the blue color of rock salt is identical with the blue obtained when sodium is dispersed electrically in organic solvents,[1] or when it is dispersed through the effects of different rays like the emanations of radium. The appearance of these blue preparations in nature is, perhaps, due to just such emanations originating in the slightly radioactive potassium salts which accompany rock salt.

It is probable that the colors of many other minerals, as those of certain precious stones, are dependent upon the presence of colloidally dispersed materials, like the colloid hydroxids.[2]

We are acquainted with a large number of other phenomena in mineralogy in which the colloid nature of the observed changes is only just becoming known. It has actually turned out that the different degrees of dispersion

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[1] See Wolfgang Ostwald, Kolloidchem. Beihefte, **2**, 438 (1911).

[2] See especially C. Doelter, Das Radium und die Farben, Dresden, 1910.

observed in different minerals may be utilized in classifying them. It was first pointed out by the lamented Austrian mineralogist, F. Cornu, that under the old heading of the "hyaline" minerals we deal with "mineral gels."[1] The existence of minerals in these highly dispersed forms is so common that Cornu was led to the formulation of his theorem of the *isochemites*, which states that there exists for every crystallized mineral a highly dispersed and therefore colloid double. Thus we know silicic acid not only in its crystalline form as quartz, but also in a gel state as opal. The latter, aside from its water content and the presence of certain impurities, is identical in composition with the former. For the hydrated crystallized iron oxid or brown iron ore we have a double in the so-called stilpnosiderite or yellow ochre; for the anhydrous crystallized red iron ore, a parallel in red ochre; for the crystallized sulphids of the heavy metal we have doubles in the highly dispersed "blacks" and "indigos" (iron black, copper indigo, etc.).

Dispersoid chemistry can also teach us much of use in the classification of the different minerals. I show you here a series of minerals all of which are composed of silicic acid alone or of this plus water (demonstration). To start with, you observe the well-known, large quartz crystals, following which come progressively smaller ones. Next stands the so-called chalcedony which no longer appears crystalline even under the microscope. Then comes cacholong, for which the same is true. Here I show you the completely amorphous, glass-like, hyalith, which already contains several percent of water. Next comes the so-called siliceous sinter (fiorite, geyserite) and then the opal which in its "soft" form contains thirty to forty percent of water. As the last member in the series, I show you a normal silicic acid gel as prepared here in the laboratory.

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[1] Nearly all the numerous papers of F. Cornu and his collaborators on the relation of colloid chemistry to mineralogy may be found in the Kolloid-Zeitschrift from the fourth volume (1909) on.

I have, as you observe, placed a series of silicic acid minerals before you possessed of widely differing degrees of dispersion, beginning as they do with macroscopic crystals and terminating with a typical colloid. *But this is just such a series of dispersoids as I have previously shown you in the case of sulphur and of sodium chlorid. But what is most important, — the properties of these minerals from the quartz to the silicic acid gel change progressively as the degrees of dispersion change.*

We have long been familiar with the fact that there exist minerals of which we cannot say definitely whether they belong in such a group as that of the crystalline quartzes or to the microcrystalline chalcedonies. Even chemical methods, as solubility in potassium hydrate, do not serve to distinguish them sharply from each other. The colloid chemist is able to show why these analytical methods must fail and why these transition forms which at first sight prove so annoying to the systematist are bound to appear. Our second lecture showed the solubility of silicic acid in alkalies to vary with its degree of dispersion, and progressively with this. In the mineral series which I have just shown you, we would, therefore, expect the solubility in alkalies to increase steadily from the crystallized quartz to the opal and the colloid silicic acid. The experiments of W. Michaelis on the solubility of quartz in calcium hydroxid support this conclusion. Under otherwise constant conditions, he observed the solubility of a smoothly polished quartz crystal to be about $\frac{10}{1000}$ percent; that of a ground crystal, $\frac{250}{1000}$ percent; that of melted quartz glass, $\frac{16}{1000}$ percent. Finely divided but still microscopically visible particles of quartz powder allowed 12.4 percent to go into solution; while from a highly dispersed quartz powder (in which the individual particles were less than 1 μ) practically any amount could be brought into solution and made to go over into chemical combination.[1]

Similar generalizations hold for the water content of the quartzes. This also increases progressively from chalced-

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[1] W. Michaelis, Koll.-Zeitschr., **5**, 9 (1909).

ony to opal. Colloid-chemically it follows as a matter of course that the water content must increase with every increase in degree of dispersion; on the other hand, it is to be expected that the absolute amount held may vary greatly, for every change in the state of the colloid (as induced, for example, through admixture with impurities) must influence secondarily the water absorption.

Through dispersoid chemistry we may, therefore, gather together certain mineral groups into "dispersoid families," the individual members of which, so far as their physico-chemical properties are concerned, pass gradually into each other.

§10.

Let me add another interesting example of the application of colloid chemistry to a mineralogical problem. Yesterday I showed you a periodic formation of precipitates in colloids, the so-called LIESEGANG rings. Many of you no doubt at the time recognized their similarity to the well-known bands and stripes which we see in such beautiful form in agates, banded jaspers, etc. Such bands are also seen at times in certain ores, like gold ores. This similarity between the two structures is more than a merely superficial one. Careful investigations of recent date, many of them the work of R. E. LIESEGANG himself, have shown that the laboratory preparations are not only identical in appearance with the corresponding minerals, but their mode of production is probably the same. We deal, in other words, in these geologic or mineralogical processes with the diffusion of molecularly dissolved substances into mineral gels, more particularly into silicic acid or silicic acid gels through which a periodic precipitation of some second substance dissolved in the gel is brought about. In other instances, as when the agate formation occurs about a central nucleus, the diffusion and the periodic precipitations may occur centrifugally. Details regarding the whole process may be found in R. E. LIESEGANG'S volume.[1]

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[1] R. E. LIESEGANG, Geologische Diffusionen, Dresden und Leipzig, 1913.

In order to show you how exactly these agate formations may be imitated in the laboratory, I have prepared the following experiment (demonstration). You will recall the periodic precipitations of silver chromate which are obtained when silver nitrate is permitted to diffuse into a gelatin gel containing potassium bichromate. If, instead of allowing the diffusion to occur in one or two directions only (as into a test tube or from a point on a gelatin-covered plate) the diffusion is permitted to occur in three directions, what I am going to show you now results. A rather large amount (say 500 cc.) of a potassium bichromate gelatin gel is prepared in a beaker and, after the whole is set, the solid mass is carefully taken out of the beaker[1] and dropped into a somewhat larger one containing silver nitrate. Silver nitrate surrounds the gelatinous mass on all sides, and therefore diffuses concentrically into it. After about twenty-four hours the silver nitrate solution is poured off, the gelatin block rinsed in water and placed upon a dish where it may be sliced open with a large, sharp knife (demonstration). If the experiment has gone well — this is always nervous work, since we cannot look into the middle of the gelatin during the experiment — the gelatin is seen to be streaked with numerous concentrically arranged bands, which yield different pictures, but all of which look strikingly like different agates.

I should like to add that we observe this type of periodic structure in many animals and plants and that a similar explanation may be given of their origin. Let me direct your attention to the volume of E. KÜSTER, which deals with the biologic applications of these periodic precipitations. Though I would not be understood as maintaining that we can at once explain the markings of a zebra or a tiger in the terms of colloid chemistry, still there is no doubt that impor-

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[1] The gel is best removed by dipping the beaker for a few moments into boiling water. If the instructions given on page 114 are followed, it is best to carry out the experiment in a refrigerator in order to obtain a thoroughly solid gel. It is necessary to use a good quality of "hard" gelatin — such as is used in bacteriology.

tant and extensive analogies do obtain between colloid chemistry and biological phenomena.

§11.

If we turn to *geology*, the important effects of weathering immediately give rise to colloid-chemical thoughts. We are here again indebted to F. Cornu for pointing out that the weathering of crystallized minerals nearly always yields gels or mixtures of gels. From feldspar we obtain the highly dispersed kaolin; from serpentine, talc; from brown iron ore, the yellow ochre, to which the yellow color of clay and earth is due.

A particularly striking example of the by-effects of colloid-chemical factors is seen in the formation of deltas. Delta formation depends upon the coagulation of grossly dispersed and colloid materials contained in the sweet waters of rivers by the electrolytes of sea water. Obviously, this coagulation will occur the more rapidly and be the more intense the more concentrated the sea water which meets the river water. It is for this reason that the unusually high salt content of the Mediterranean has yielded the most famous example of delta formation, namely, that of the Nile.

§12.

Soil chemistry has also to do with many different dispersoids, of which those that are highly dispersed — more particularly colloidally dispersed — are especially important. What are known as mechanical methods of soil analysis are nothing but methods of dispersoid analysis — coarsely dispersed particles are separated from more finely divided ones by sieving, by sedimentation and by filtration. The colloidally dispersed phases are then separated from each other by dialysis; the molecularly dispersed, by processes of diffusion.

Of the typical colloids or their gels which we find in soils, four kinds deserve particular mention, namely, silicic acid and the silicates, aluminium hydroxid and its compounds with silicic acid (in other words, the clays, etc.), iron hydroxid, and those substances rich in carbon and of unknown chemical composition, summed up under the term of the humus acids, and a part of which at least are undoubtedly colloid.[1] To this list must be added the micro-organisms of various kinds — like the soil bacteria — of which many are so small that suspensions of them show coagulation phenomena.[2] We must also add the mucinous substances which are secreted by such soil organisms.

For determining the colloid content of different soils, use has recently been made not only of dialytic procedures but of the adsorption of dyes like malachite green.

The important rôle of the colloids in the soil has been more and more emphasized during the past few years — it has in fact been maintained by some that "the fertility of the soil is proportional to its colloid content." This is certainly carrying it too far, as best shown by the fact that a whole series of methods for improving the soil consists in producing a coagulation of the soil colloids. The good effects of frost upon a soil are probably due to such a coagulation. Laboratory experiments show that during a frost

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[1] For a discussion of the colloid or non-colloid nature of the humus acids — a discussion not yet ended — see the extensive review of H. Brehm, Koll.-Zeitschr., **13,** 19 (1913). According to S. Odén [Arkiv. f. Kemi. usw., **6,** Nr. 26 (1912); Koll.-Zeitschr., **14,** 123 (1914); Kolloidchem. Beihefte, **11,** 76 (1919) where references to the literature may be found] the humus acids or alkali humates obtained in the usual fashion from peat are non-colloid for they dialyze, show no ultramicroscopic structure, are not precipitated by salts, are adsorbed with difficulty, etc. These same substances separated in similar fashion from loam by Professor Suzuki, working in my laboratory, behaved in typical colloid fashion. They dialyzed but little, showed a distinct ultramicroscopic structure, were easily precipitated by sodium chlorid, were readily adsorbed by bone black, etc. These facts corroborate the general experience of chemists that the humus substances may appear in all degrees of dispersion and that the much discussed question of whether they are "colloid" or "molecular" cannot be answered by yes or no. This question carries a different answer under different circumstances.

[2] According to E. Hilgard, A. Atterberg, etc., quartz suspensions begin to show coagulation phenomena when their particles attain a size of 20 to 200 μ. In this connection, and for a general discussion of the relation between colloid chemistry and agricultural chemistry, see P. Ehrenberg, Koll.-Zeitschr., **3,** 193 (1908); **4,** 76 (1909); **5,** 100 (1909).

gels are formed which decrease a soil's "richness." We may explain similarly the good effects of "burning" a soil, a practice much followed formerly. Under this heading is also to be put the application to the soil of such strongly coagulating salts as calcium sulphate. All these methods not only bring about a coarsening of the soil colloids, but they reduce their high indices of swelling which constitute the characteristic element of excessively "rich" soils. These facts should suffice to show that too large a colloid content does not represent the optimum for plant growth.

On the other hand, it cannot be doubted that the colloids are not only important, but that they are absolutely essential to the fertility of soil. This was well known even to the old agricultural chemists and is proved directly by the knowledge that sandy or gravelly soils — be their chemical composition what you will — are unfertile. A whole series of facts serves to emphasize the importance of a medium content of colloid materials. The water content of soil must obviously be largely regulated through the presence of hydratable colloids. Sandy or other coarsely dispersed soils do not hold rain; neither do they draw up water from the depths as readily as do soils containing more colloid material. The soil colloids, by holding the water which falls upon them and by bringing it up from the depths, fulfill one of the most important conditions necessary for the growth of plants upon the surface of our earth.

But the adsorption power of the soil colloids for dissolved substances is also of tremendous importance. Agricultural chemistry recognizes this in two directions. There is, first of all, the adsorption of nutritive substances necessary for the growth of the plants; on the other hand, there is the adsorption of materials which are poisonous to plants, or which are the product of their metabolic processes. Water plants do better, for example, when any highly dispersed powder or colloid, such as carbon, iron hydroxid or silicic acid, is added to the water.

The adsorptive activity of the soil colloids so far as nutritive substances is concerned may be either useful or pernicious, depending upon the concentration of the substances present and the intensity of the adsorption — the latter increasing, other things being equal, with the increase in colloid content. This adsorptive activity has a favorable action when the nutritive substances concerned are present in relatively low concentrations. They are then gathered together by the soil colloids and brought to the plant in greater amounts. On the other hand, it may be followed by evil consequences, as when the concentration of the nutritive substances thus brought about exceeds an optimum — an effect particularly likely to be produced in the case of the salts — or when the adsorptive force is so great that the nutritive substances are held too firmly by the soil colloids so that the plant roots can no longer take them over in optimum amounts, or at an optimum rate. The good effects of using calcium salts after fertilizing soil with phosphates depends in major portion upon the coagulating effects of the former, which thereby antagonize the adsorption of the phosphoric acid by the soil colloids. Unfavorable adsorption effects undoubtedly come to pass when the soil contains too much colloid material. These equilibrium considerations lead to the same conclusion which the practical workers in agriculture have so long held. *Under otherwise constant conditions, a medium colloid content gives greatest fertility. But this medium colloid content may have different absolute values, depending upon the concentrations of the nutritive materials present — in other words, depending upon the chemical composition of the soil and the individual needs of different plants.* It seems to me that this view best coördinates the numerous and apparently contradictory findings of different students of the question covering the relationship between soil colloids and its fertility.

In passing I should like to mention the interesting chemical consequences, like the so-called *adsorption decompositions*, which often follow adsorption in soils. Many years ago, J. M. van Bemmelen showed that gels absorb the potassium from potassium sulphate solutions and not the sulphate — this being followed by the appearance of free sulphuric acid in the solution undergoing adsorption. These specific adsorption phenomena which in their turn may be followed by tremendous secondary chemical changes undoubtedly play a great rôle in the dynamics of the soil.[1]

§13.

I have already used up the major portion of lecture time and yet am only now coming to perhaps the greatest and most interesting of all the scientific applications of colloid chemistry. I refer to those made in biology and medicine.[2] Colloid chemistry is the promised land of the biological scientist, and it is almost impossible for the enthusiastic colloid chemist not to become poetical in this region.

As you know, the elements necessary for life may be gathered together under the chemical headings of the proteins, the lipoids, the salts and water; but the physical and the physico-chemical conditions necessary for life cannot be more accurately or more concisely summed up than in the words *all life processes take place in a colloid system.* The colloid state is the means of integrating biological processes. More correctly expressed, only those structures are considered living which at all times are colloid in composition.

It is self-evident that because of the close association between colloid chemistry and biology the number of in-

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[1] The relations of agriculture to colloid chemistry are detailed in the extensive volume of P. Ehrenberg, Die Bodenkolloide, 2te Aufl., Dresden, 1918, as well as in the shorter but highly to be recommended text of G. Wiegner, Boden und Bodenkolloide in Kolloidchemischer Betrachtung, Dresden, 1918, a second edition of which is in preparation.

[2] It is impossible to list a series of papers which will cover adequately the many relations of colloid chemistry to biology and medicine. For a first orientation in this field, see H. Bechhold, Colloids in Biology and Medicine, trans. by Bullowa, New York, 1919, where numerous references will be found. The physical peculiarities of living matter with due emphasis upon its colloid nature are discussed in L. Rhumbler, Das Protoplasma als physikalisches System, Wiesbaden, 1914. Larger volumes dealing with this general subject are those of R. Höber, Physikalische Chemie der Zelle und Gewebe, Leipzig,

dividual colloid-chemical laws which hold in biology must be enormously great, for since organisms are merely special instances of colloid systems, there can exist no biological problems in which colloid chemistry must not play some part. The colloid-chemical point of view permeates biology from its beginnings in causal morphology to its endings in chemical physiology. Bacteriologists, physicians, students of experimental morphology, plant physiologists, all are interested in colloid chemistry and its development. The biologists find colloid chemistry useful to their ends as is no other science. It has not, however, been pressed into their hands ready-made; from the earliest days they have themselves furthered the principles of pure colloid chemistry and then applied them to their specific problems. Nothing demonstrates better the close relations between the two sciences than the fact that a large number of colloid chemists entered their fields from biology or through biology. I need but mention A. Fick, C. Ludwig, F. Hofmeister, Wo. Pauli, W. M. Bayliss, M. H. Fischer and F. Bottazzi. And even the newest chapters in colloid chemistry are indebted for their rapid and magnificent growth in no small fashion to the interest and enthusiastic coöperation of the biological colloid chemists.

§14.

I choose arbitrarily when from the wealth of the biological applications of colloid chemistry I select a few examples.

Let us begin by asking how it is proved that living substance is itself colloid. Chemical analysis shows that the characteristic building block of organic material is protein.

1912; N. Gaidukow, Dunkelfeldbeleuchtung in der Biologie, Jena, 1911; F. Bottazzi, Handbuch der vergleichenden Physiologie, Jena, 1913. A particularly important volume is that of Martin H. Fischer, Œdema and Nephritis, 3d edition, New York, 1921, in which not only medical but many non-medical problems of biological interest are discussed; see also his Fats and Fatty Degeneration, New York, 1917, and his Soaps and Proteins, New York, 1921.

But, as my previous lectures showed, it is this very substance which is most typical of the colloids, belonging, as it does to the class of the hydrated emulsoids. The fact that great numbers of experiments in colloid chemistry are made with fresh egg albumin, with blood serum, with muscle juice, indicates that the proteins exist in colloid form in the living organism and that they are not "produced" by chemical methods. Moreover, it is possible to coagulate all or parts of a living cell (like the flagellæ of bacteria), and the means employed to this end and the results obtained are identical with the coagulation of proteins in test tubes. Finally — and this is perhaps the simplest direct proof of its colloid nature — living matter may be studied under the ultramicroscope. This experiment can, however, not be carried on very long, for the intense light needed soon kills the organism with the exhibition of the signs of coagulation. When the colorless plasma of an alga cell[1] is thus studied, it is seen to consist of a mixture of numerous particles of different sizes, of which a large number are typically colloid. It is of special interest that many of these particles are in active motion. The particles approach each other, separate, coalesce to form larger particles, disappear entirely — indeed he who observes this ultramicroscopic picture of a living cell for the first time will perhaps be inclined to hold that the "true" life of any cell is not to be seen except ultramicroscopically. In this he is to a certain extent at least in error, for the movement of the colloid particles in living matter is nothing more than the same movement as observable in any sol showing Brownian movement. The ultramicroscope shows the plasma of living cells to be a *mixture of hydrosols* of different degrees of dispersion. This conclusion, therefore, bears out the results of chemical analysis. There is, moreover, no contradiction between this finding and the fact previously emphasized that ultramicroscopic analysis often fails to establish the colloid character of the biocolloids. This is because of their great hydration.

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[1] See N. Gaidukow, Dunkelfeldbeleuchtung in der Biologie, Jena, 1913.

It may now be asked whether this mixture of hydrosols exists in a form in which the dispersed particles, like the proteins or lipoids, float about in the dispersion medium, or whether through secondary rearrangement these colloid particles may go to form microscopically visible structures. The biologists among you will be well aware that a union of particles into a network or a honeycomb is often seen in living protoplasm. There are some authors — as O. Bütschli — who have held that such a subcolloid structure is characteristic of all living matter. Can the colloid-chemical laboratory explain how such microscopic structures come to pass in living protoplasm? It can. N. Beijerinck discovered the interesting phenomenon that when two liquid colloids like gelatin and starch are mixed in definite concentrations, the resulting mixture of hydrosols does not show the particles of the two to be dispersed in colloid form uniformly throughout the liquid but that one of the colloids divides itself in droplet form into the second. The mixture in consequence assumes a net or honeycomb-like appearance. The structure thus produced is obviously analogous to that seen in living matter when studied microscopically or ultramicroscopically.

§15.

A question much discussed in general biology and answered through colloid chemistry asks regarding the physical state of living matter. Is protoplasm solid or liquid? Time has shown that the form of this question is again a wrong one. Protoplasm is neither solid nor liquid when compared with typical solids or liquids. Its physical peculiarities are those of a hydrated emulsoid which may show all degrees of fluidity ranging from those values which, on the one hand, are characteristic of a normal liquid to those which, on the other, are characteristic of a solid. As gelatin, depending upon its temperature and its concentration, may show all states from a liquid to a solid, just so may protoplasm. As a dilute gelatin gel — and we shall see shortly that living protoplasm is just such a dilute colloid —

unites within itself the properties of a liquid and of a solid, just so does living matter show properties which at one time make us think it fluid and at another solid. Protoplasm shows, for example, capillary phenomena, protoplasmic streamings, vacuole formation, throws out pseudopods, and its separated portions form droplets.[1] All these are the properties of liquids. Upon the other hand, protoplasm shows a plasticity and a maintenance of form which is seen only in solids. An ameba deformed through pressure tends gradually to resume its spherical form; and slight but persistent pressure will give the embryonic cells of frog eggs some other than a spherical shape, and this will persist for hours.

It would seem that living matter is constantly oscillating between the extremes of a solid gel and a liquid gel. Such oscillations probably underlie ameboid motion and are the cause for the appearance and disappearance of the numerous structures seen at different times in the life cycle of the cell. The German investigator L. RHUMBLER, who has studied the physical properties of living matter in masterly fashion, came to the conclusion that only a specially dispersed structure — a "spumoid" structure, as he calls it — can account for this remarkable combination of physical properties. He himself emphasizes, however, that this structure must be of the same kind as that possessed by any hydrated emulsoid. In reality the physics of the two is the same.

§16.

Closely related to the physical properties of living matter is its great *water content*. It is not generally recognized how very great is this proportion of water in living matter. More than half our body weight, for example, is water and marine algæ and jelly fish hold as much or more than ninety-six percent. It is certainly remarkable that these organisms not only hold their shape, but move, swim, eat

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[1] See L. RHUMBLER, Das Protoplasma als physikalisches System, Wiesbaden, 1914.

✓ and make love — and this with ninety-six percent of water in their affection. These things are made possible through colloid chemistry, for only colloid systems — in other words, the gels — can hold their shape when thus rich in water. These remarks explain why the biological question of how this water-holding power is brought about and how it is regulated under different circumstances becomes a problem in colloid chemistry.

No doubt you know that in the heydey of the classical physical chemistry of the solutions, other and non-colloid, namely, osmotic forces, were called upon to explain the absorption and the movement of water in organisms. It was assumed that the cell membranes found in the tissues of the higher animals acted as osmotic membranes in that they gave passage to water but did not permit dissolved substances like the various salts to pass through them. In this way through concentration differences an osmotic movement of water was brought about into the cell and thus its cell turgor was maintained. The modern developments of cellular physiology have shown more and more clearly that this *rôle of the osmotic forces has been greatly overestimated.* It may now be said that there exist but exceptional instances in which may be discovered any fairly complete analogy between the laws of osmotic pressure and those which govern the absorption of water by a cell. Even though I would not hold to the extreme view that osmotic processes play no rôle whatsoever in the processes of water absorption by living organisms, unprejudiced consideration of the facts compels the conclusion that besides these, or better expressed, far transcending these in importance, entirely different forces determine the water content of an organism. *Not the osmotically active, molecularly dispersed constituents of a cell (more particularly the salts therefore) but the plasma colloids are primarily responsible for the water content of the living organism and for the changes which this shows.*[1]

[1] Important new work bearing on this question is that of W. von Moellendorff, Koll.-Zeitschr., **23**, 158 (1918) who shows that osmotic processes (in

Looked at *now* this conclusion, which in broad form was first drawn and discussed by MARTIN H. FISCHER,[1] seems almost self-evident. For not only do we know from laboratory experiments that the emulsoids obtained from living organisms are able to hold enormously large amounts of water just as can the living organisms themselves, but we know also that this capacity for holding water, as measured, for instance, through viscosity changes, can be tremendously modified by apparently trivial and widely different types of changes in surroundings. The influence of electrolytes (such as acids, bases and salts) is so great that variations in their concentration *within biological limits* results in marked variations in the water content. I should like to emphasize this by citing an example. As I have already shown you, acids in moderate concentration increase tremendously the amount of water absorbed by gelatin, fibrin or egg albumin. The influence of the hydrogen ion is so enormously great that the presence of even such a "weak" acid as carbonic acid brings about a distinct increase in swelling. As WO. PAULI and R. CHIARI have shown, the amount of water absorbed by a gelatin plate which is kept in freshly distilled water is much less than that of one kept in a distilled water exposed to air containing a little carbon dioxid. This increase in swelling may be used as an indicator for the presence of hydrogen ions. These things show, at the same time, how very easily, through variations in the chemistry of living organisms, changes may be brought about in living matter which will alter its water content. We shall return to this question shortly.

so far as they appear at all) can come to pass in certain types of cells only *within their bodies.* The osmotically active "membranes" are to be looked for in the surfaces which separate the droplets of hydrated biocolloid from the cell sap. But this "microösmosis" or "dispersed type of osmosis" will probably not follow the classical and simple laws of osmosis as observed in macroscopic systems but exhibit transition characteristics tending to class it with the phenomena of swelling and hydration.

[1] See the literature cited in the footnote on page 166.

§17.

Besides these structural and physical peculiarities common to living matter which are newly illuminated or explained through colloid chemistry, there exist many close relations between colloid chemistry and the more purely chemical and physico-chemical reactions which are characteristic of living matter. It has often been asked, for example, how it is possible that so many different reactions may take place side by side in a cell (a structure which consists so essentially of liquid) without all running together and yielding chaos. The experiments with colloid mixtures mentioned above show that two colloid substances — even when divided into the same dispersion medium — need not mix with each other, but can continue to exist side by side in the form of microscopic droplets. The great variety of microscopic and ultramicroscopic structures observable in living matter leads to the conclusion that the different chemical constituents of the protoplasm — more particularly those existent in colloid form — may in similar fashion exist side by side without mixing. As F. Hofmeister has indicated, we may imagine each of the individual droplets to be a tiny, special laboratory, in which, undisturbed by the surroundings, some one or certain few reactions take place. Such a localization of chemical processes within the mixture would be aided by the fact that a large part of the reacting substances and of the reaction products are colloid and therefore do not on their own accounts tend to diffuse and so mix themselves with neighboring substances.

§18.

But the colloid state plays a great rôle in the chemistry of living matter in yet another direction. We have repeatedly emphasized that adsorption processes must play a great rôle in catalysis, that, in fact, many of its features must be held to be the direct consequences of concentration increases brought about in surfaces. A colloid mixture of the type of protoplasm must therefore offer peculiarly favorable conditions for the play and for the acceleration of chemical reactions. It is consequently not to be wondered at that those substances which are to be counted among the most fundamental of the constituents of living matter, namely, the ferments, are known for the most part only in colloid form. Living matter seems to be a meeting ground for adsorption effects and colloid catalyses.

Allow me, after this general survey, to touch upon a series of special biological problems in which the colloid-chemical point of view has brought much light. The choice must again be arbitrary and my review most superficial. For further details I direct you to the special articles which deal with these problems.[1]

§19.

Colloid chemistry brings us light in even those first of all biological processes which are concerned with the formation of new organisms, namely, the phenomena incident to fertilization and the early development of the embryo. You perhaps know that the stimulus to the development of a sea-urchin egg, for instance — it matters not whether this be brought about by sexual fertilization or by so-called artificial means — is characterized morphologically by the formation of a so-called astrosphere. Rays of concentrated plasma appear either in the immediate vicinity of the nucleus of the fertilized egg, or, it may be, in other portions of the egg plasma. These rays then act as centers toward which the products of the divided nucleus move. I cannot go into details, but in spite of the specific variations which appear in different animals, what I have described is constant in all fertilization and cell division.

Closer study of the problem proves that this formation of the astrosphere represents a special form of coagulation of the plasma colloids, and microscopic observation suffices to

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[1] See the second footnote on page 165, as well as numerous articles in the Kolloid-Zeitschrift in which references to other striking papers may be found.

show that we are dealing with a localized collection of water-poor and coarsened plasma. We deal, in other words, with the conversion of a sol into a gel. Micro-dissection proves this without the question of a doubt, for the astrospheres may be pulled, as more solid masses, out of the relatively fluid egg plasma (G. L. KITE, R. CHAMBERS).

The conclusion that this phase of fertilization represents a coagulation process may be proved by yet other means. Those of you who have followed the well-known studies of JACQUES LOEB and of other investigators of the problem of artificial parthenogenesis will know that the unfertilized eggs of sea-urchins or star-fish may be made to develop by many different means. Not only does treatment with acids, alkalies or specific ions lead to this result, but the water extraction incident to the effects of neutral salts is also effective. Temporary exposure to high and low temperatures, exposure to other colloids (as the serum of higher animals), treatment with organic liquids like benzol or toluol and even mechanical treatment (such as shaking, rubbing or brushing) accomplishes artificial development in the unfertilized eggs of many organisms. What have all these methods in common? If you will recall what I said yesterday regarding the alterations in the colloid state that may be brought about through trivial external changes, it will be clear to you that all these methods for inducing artificial parthenogenesis are such as lead to changes in the colloids — more especially to their coagulation. *All the listed methods, to which more might be added, leading to the development of an egg, serve also to produce coagulation in protein sols.* Conversely we may say that we hardly know a method of producing such protein precipitation which when properly used may not also be employed to start artificial development.[1]

This coagulation theory of fertilization receives pretty support through the possibility of causing in colloids and colloid mixtures a localized and oriented coagulation which

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[1] MARTIN H. FISCHER and WOLFGANG OSTWALD, Pflügers Archiv. f. d. g. Physiologie, 106, 229 (1905).

in structure is strikingly like the astrospheres observed in developing cells. Fig. 42 is a picture of such an artificially produced astrosphere taken from the work of O. Bütschli and made at a time when the colloid-chemical theory of fertilization which I have sketched to you had not yet been born. The biologists among you will grant its striking similarity to the real thing.

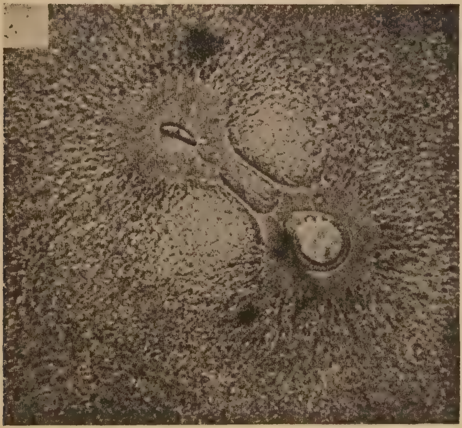

Fig. 42.

The primary process which leads to development in an egg is seen, therefore, to be a colloid-chemical one and of the nature of the transformation of a sol into a gel. But please do not misunderstand me in the matter. I would not have you think that this explains everything that there is to the process of fertilization. Many different chemical processes, as those of increased oxidation, for example, accompany the astrosphere formation, but these appear only after the colloid changes which I have described have started the process. That which starts development is colloid-chemical.

But not only is the beginning of development in a metazoon egg capable of a surprisingly thorough experimental colloid-chemical analysis but so is the process of cell division and the increase in the number of cells in unicellular organisms.

The experiments of J. Spek[1] need special mention in this connection. This investigator has shown that the rate of multiplication of infusoria (paramecia) can be greatly increased, ten to twenty times in fact, through the addition of salts which like lithium chlorid favor swelling; salts like the sulphates, on the other hand, which inhibit swelling decrease the rate even when added in amounts not toxic. Even so complicated a phenomenon as that of gastrulation Spek found to be capable of theoretical and experimental colloid analysis on the assumption that the phenomenon is essentially one of swelling. In fact this enthusiastic investigator seems to have utilized this single colloid-chemical change perhaps too exclusively and so ignored, for example, other simultaneously possible colloid changes as the coagulative phenomena already referred to above.[2] One needs to bear in mind that protoplasm represents a mixture of colloids and that one and the same electrolyte for example may act in exactly opposite fashion upon two different colloids, producing the flocculation (dehydration) of one, while making a second swell.[3] It is necessary to emphasize these facts in order to make sure that a just appraisal is made of the importance of each of the various colloid-chemical changes that may play a rôle. It represents, however, a happy state of affairs when it is seen that differences of opinion exist between workers only as to the relative values to be attached to various colloid-chemical changes in the analysis of a biological phenomenon; that the biological phenomenon is a problem which involves only colloid changes — this none of the workers doubts.

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[1] J. Spek, Kolloidchem. Beihefte, **10,** 259 (1918); **12,** 1 (1920) where references to the literature may be found.

[2] I hope at another time to bring proof for this conclusion publicly; thus far I have done so only in correspondence.

[3] The phenomenon of "cloudy swelling" as observed in the cornea may be cited as an example. According to the investigations of Martin H. Fischer cloudy swelling results from the action of an acid (or a similarly acting substance) simultaneously but in opposite directions upon different corneal colloids. See the text further along.

§20.

Swelling phenomena also play a large part in the various phenomena characteristic of *growth.* Chemical analysis shows frog larvæ, for instance, to owe their enormous changes in weight up to the time of their metamorphosis to land animals to mere changes in the amount of water absorbed. As shown in the curves of Fig. 43, the increase in amount of solid substance is so slight that at the time when the frog takes to land, it consisto of ninety-three percent of water.

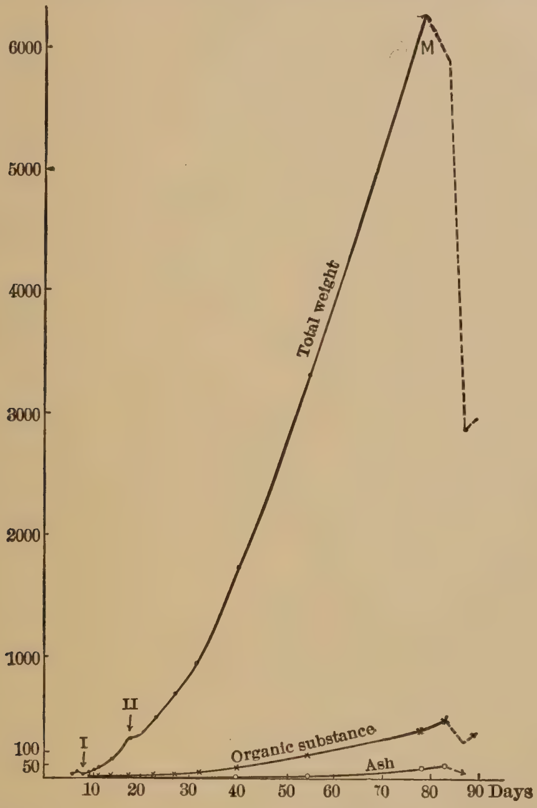

Fig. 43. — Increase in weight during growth of frog larvæ.

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[1] See A. Schaper, Arch. f. Entwicklungsmechanik, **14,** 356 (1902); also Wolfgang Ostwald, Über die zeitlichen Eigenschaften der Entwicklungsvorgänge, 49, Leipzig, 1908.

These same facts hold for the growing parts of plants. A change in the osmotically active constituents of a growing part great enough to account for these enormous water absorptions is unknown. We know, however, that the growing parts of many plants are acid. But as previously pointed out, acids enormously increase the water absorbing powers of various colloids even when present in only minimal concentrations. These things point clearly enough to the importance of swelling phenomena in growth processes.

When the developing frog becomes a land animal, it loses much water. But this may also be explained colloid-chemically, for, as I have previously emphasized, a gel under ordinary experimental conditions has a different and lower swelling point when in equilibrium with water vapor than when in equilibrium with fluid water. Colloid chemistry is also interested in the fact that desert plants often show an acid reaction — a circumstance which would permit them not only to take up more water, but also to hold better such as has been absorbed against the forces leading to drying. The diurnal changes in the reaction of plants are probably also followed by similar variations in water absorption capacity.

§21.

Another problem to the solution of which colloid chemistry has been called is that of the nature of the *muscular contraction.* I cannot go into details, but I should like to point out that the electrical, chemical, mechanical, optical and other changes incident to the muscle contraction can all be best understood in the terms of colloid chemistry.[1] The essence of the muscular contraction seems to reside in a

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[1] See Martin H. Fischer and W. H. Strietmann, Koll.-Zeitschr., **10,** 65 (1912); also Wolfgang Pauli, Kolloidchem. Beihefte, **3,** 361 (1912) and the recently issued monograph of O. von Fürth, Ergebnisse der Physiologie, Wiesbaden, 1920. To von Fürth's list of references should be added that the first quantitative studies on the effects of acids in bringing about the swelling of gelatin date from Wolfgang Ostwald, Pflüger's Arch., **108,** 563 (1905).

transport of water from certain of the structural elements making up the muscle to certain other contractile elements. Differently expressed, a migration of water occurs from one colloid to a second making up this tissue. This migration is brought about through a production of acids (more especially of lactic acid) in the muscle. In this we see again the so-widely distributed and so exceedingly active influence of the hydrogen ions upon water absorption by a biocolloid. That the phenomena of swelling as observed outside of the body may occur with a rate and to an extent demanded by a colloid-chemical theory of the muscle contraction — this I showed you yesterday in discussing the swelling of gutta-percha leaves and of gelatin. In discussing swelling I also emphasized that an amount of mechanical energy is liberated which is entirely adequate to explain the mechanical phenomena incident to the contraction of a muscle.

§22.

Of the many other problems in physiology which seem accessible to colloid-chemical analysis, I can only touch upon that of *secretion.* The physiologists among you will know that what physiology seeks is an understanding of the nature of the "driving" forces which bring about the secretion of water by a cell or tissue — at times even against the existence of a counter-pressure like hydrostatic or osmotic pressure. Perhaps more than in any other chapter of physiology do we in this problem of secretion still speak of "vital" forces. Even after utilizing the newest concepts of physical chemistry in addition to the older ones of filtration, diffusion, etc., we still have much left to be explained. Here again, colloid chemistry is acquainted with forces which, so far as we can see, are fully able to meet the requirement that the forces producing secretion must be essentially independent of hydrostatic and osmotic pressure differences, while it makes clear at the same time the nature of a number of the phenomena which commonly accompany such secretion. I refer to the phenomena of secretion observable in simple colloids, and discussed in the last lecture under the heading of syneresis.

I ask you to recall that every secretion springs from a colloid matrix, and that the secretion contains not only water but colloids and salts and these of the kind present in the secreting tissues themselves. Even the most watery of the secretions, like the urine, contains a series of non-dialyzable substances, the so-called "colloid nitrogen." What is true of secretion is also true of syneresis. The serum squeezed off contains not only water but also colloids and salts and these in proportions which need in no sense be identical with those existent in the secreting gel. In syneresis in colloids, as in physiological secretion, both the amount and the composition of the serum given off varies not only with the kind of colloid but with the kind and the amount of the material contained in it, etc.[1] But what is most important is that the syneretic secretion of fluid is not determined through osmotic or hydrostatic pressure differences, but is dependent upon forces existent "within" the gel itself — upon forces, in other words, which lead to changes in its "internal state." With these suggestions I must let the matter rest.

§23.

Another physiological problem much studied recently is that of *vital staining*, in other words, the taking up of dyes by living cells. It has become increasingly evident that the degree of dispersion of the dye is a factor of prime importance in bringing about positive results.[2] As a rule only molecularly or highly dispersed dyestuffs can be taken up, the plasma film surrounding cells seeming to act like an ultrafilter.

[1] See the footnotes on pages 98 and 99 as well as the accompanying text.

[2] See especially W. Ruhland, Koll.-Zeitschr., **12**, 113 (1912); **14**, 48 (1914), where the literature is cited; also the papers of W. Schulemann and W. von Moellendorff in the more recent volumes of the Kolloid-Zeitschrift.

I would like to add a word here regarding our methods of fixation and staining of dead tissues. Some twenty years ago the biologists were much frightened when the botanist A. Fischer pointed out that many of the structures found after such treatment are "artifacts." Fixing and staining reagents bring about dehydration and coagulation effects — in other words, colloid-chemical changes — in the state of the tissue colloids. It is undoubtedly true that many things may be seen in such fixed tissues which it would be wrong to say exist in living protoplasm; on the other hand, it would be just as wrong to hold that such fixation methods can tell us nothing whatsoever regarding the structure of living matter. A rational fixation and staining technique can apprise us of the character of the changes wrought by fixation and staining reagents in test tube experiments upon such highly hydrated mixtures as are presented by the biocolloids; and it is perfectly safe to apply the conclusions won in this fashion to the related problems of histology and biology. The comparative experiments of this type which have been made in masterly fashion, for example, by G. Mann,[1] and more recently by R. E. Liesegang form the foundation stones of a rational histology. Obviously even the normal microscopic structure of living tissues is the result of changes in state of the biocolloids, wherefore detailed study of these, such as is presented by protein sols in a test tube or on a slide, can in this fashion be used for the interpretation of the ways and means by which normal structure is produced.

§24.

These and associated colloid-chemical studies serve in this way to contribute to a science of which, I admit, I speak with reluctance, even though it is the crown of all biology. I refer to *synthetic biology*, the science of the artificial production of living things. Since the synthetic

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[1] G. Mann, Physiological Histology, Oxford, 1902; see the review of this book in Koll.-Zeitschr., **2**, 153 (1907).

production of urea by Liebig and Wöhler, we have been familiar with a *synthetic biochemistry.* It is today an easy matter to produce in the laboratory substances and reactions which are commonly seen only in living organisms. By comparison we are still much in the dark regarding a sister science, that of *synthetic biophysics.* Even when we succeed in producing ameboid movements in drops of liquid or in colloid mixtures, or when we discover methods whereby non-living matter can be made to build protective coverings for itself, to exercise choice in the taking up of nutritive materials, we incline to call these analogies to biological processes "imitations" of the processes and thus to cheapen the value which we set on them. *But such experiments are experiments in synthetic biophysics and of exactly the same significance as the synthesis of urea or catalysis by colloid metals for synthetic biochemistry.*

Like the chemistry of organized substance, so must its physics be analyzed into unit processes and through gradual rebuilding from these be resurrected into a synthetic biology. Trustworthy results will, of course, be obtained only through systematic study. It would be most unscientific, for example, to call certain precipitates primitive organisms because they look like such. A synthetically produced organism must, naturally, show *all* the fundamental characteristics of organized matter at one and the same time. But in spite of the great distance still to be traversed before such a goal is attained, there can be no doubt that through a proper combination of individual chemical and physical processes of the types observable in organisms, the attempt to reach such a goal represents an entirely scientific problem. In the still much-neglected biophysics of the colloids there is already at hand a wealth of suggestive material.

§25.

I must in conclusion give you a hasty view of the applications of colloid chemistry to *medicine.* Obviously the number of possible applications here is just as great as in the biology of the normal organism, for pathological changes, too, take place only in that colloid foundation in which all normal life processes occur. Just as normal causal biology must be edited — must be rewritten, in fact — in the terms of colloid chemistry, even so must *pathology* be rewritten. Time does not permit me to enter into many details, but a few interesting examples will illustrate my point.

Closely associated with the general problem of how an organism holds its normal water content is that of the ways and means by which it holds more than this, as is the case in the pathological phenomena of *edema* and its various clinical subheadings. As in the case of the normal absorption of water by the normal organism, the tissue colloids again play a chief rôle in this pathological problem as demonstrated in the fundamental investigations of MARTIN H. FISCHER.[1] Changes in the water-holding capacity of the tissue colloids are responsible for edema and an abnormal production or accumulation of acids in the involved tissues again appears to be the main agent favoring the swelling, even though it is possible that the hydrating effects of other substances like the proteolytic ferments (W. GIES) may also act in this direction. An abnormal production or retention of acids can be assumed or proved to be the primary, etiologic cause in most cases of edema. Acids are produced, for example, whenever the normal processes of oxidation are inhibited, as through the presence of different poisons, through a shutting off of the circulation (passive congestion), through anatomical changes in the organs necessary for the maintenance of a proper circulation, or when in consequence of a flea bite or a bee sting formic acid is introduced locally into a tissue. Experimentally "artificial flea bites" can be produced very

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[1] See the numerous papers of MARTIN H. FISCHER and his collaborators in the Kolloid-Zeitschrift and the Kolloidchemische Beihefte as well as his Œdema and Nephritis, third edition New York, 1921.

nicely by pricking a gelatin plate with a needle dipped in formic acid and then placing the gelatin plate in a little water (demonstration).[1]

The correctness of the view that the water-holding property of the colloids and changes in their state determine both the normal and the pathological water content of tissues can also be demonstrated in the following fashion (demonstration). I have left untouched the experimental apparatus with which I showed you the influence of electrolytes upon the swelling of gelatin. I have merely placed in the different solutions beside the gelatin discs, whole organs, sheep eyes, frog legs, etc., and have left them there for a number of hours. If you will look at these experiments you will note that the influence of these different electrolytes upon the swelling of these organs parallels completely the influence of these same substances upon the swelling of the gelatin discs. You note that in the acid and in the alkali there is an enormously greater increase in the size of the organs than in the pure water — in other words, they have absorbed more water in the acid and alkali than have the organs left in the pure water. On the other hand, where a proper salt has been added, a distinct shrinkage has occurred (Fig. 44). When we touch the organs which have swelled in the acid we become conscious of the same feeling which edematous organs give us.

In passing let me emphasize that just as the addition of salt to gelatin or fibrin swelling in the presence of an acid reduces the amount of the swelling or suppresses it entirely, just so has this principle been successfully employed in the reduction of clinical forms of edema.[2]

It has been argued against this colloid-chemical theory of edema that it does not suffice to explain how the excessive accumulations of fluid which are often found be-

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[1] See Martin H. Fischer, Œdema and Nephritis, third edition, 241 and 733, New York, 1921.

[2] See the papers and books of Martin H. Fischer and his collaborators. See also Martin H. Fischer, Kolloidchemische Beihefte, **4**, 343 (1913).

tween the cells and in the body cavities are to be explained. But this phenomenon whi chwe are wont to see particularly in the latter stages of edema, is also easily explained colloid-chemically. The spontaneous secretion of such liquids, which, as you know, are often rich in albumin, is the analogue of what we call syneresis in colloids and may be expected to appear in particularly marked form whenever the gels from which they are squeezed off are particularly rich in water. As I pointed out before, the amount of fluid thus squeezed off by any hydrophilic colloid like gelatin increases with increase in the water content of the gel.

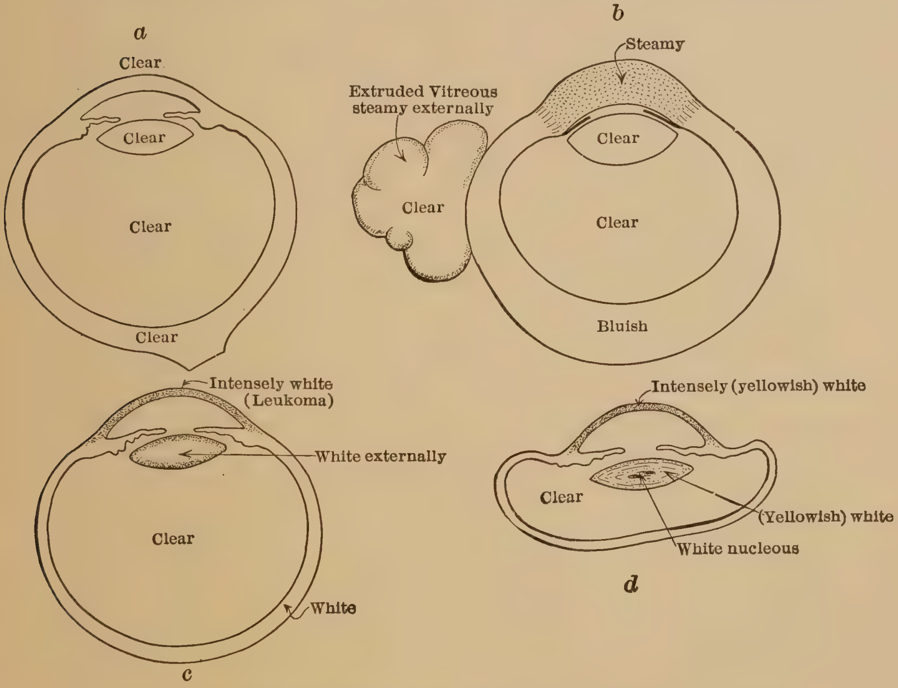

FIG. 44. — Swelling of sheep eyes according to MARTIN H. FISCHER.
(*a*) the normal eye
(*b*) in HCl
(*c*) in HCl plus $Mg(NO_3)_2$
(*d*) in HCl plus $FeCl_3$

Less just still is another objection which has been raised against FISCHER's theory of edema. It is pointed out that the concentration of the "free" acid or of the "free" hydrogen ions is rarely higher in edematous tissues or fluids than in normal ones because, as generally held, the organism regulates the "reaction" of its tissues through buffer mixtures, etc. This objection is to be answered by saying that the increased water absorption is *of course* not to be attributed to any "free" acid which may be found but, contrariwise, to the "non-free" acid, in other words, to the acid which has been bound by the tissues. Only the electrolyte *bound* to a colloid either through adsorption or chemical union can alter its state. The nature of the equilibrium between the bound acid and the free is still a question which requires quantitative study. If it is assumed that in the low acid concentrations involved we are dealing with adsorption then we get an immediate explanation of why union with a relatively large amount of acid goes hand in hand with the presence of only a minimal amount of free acid; for in low concentrations, as you know, adsorption is practically complete. It needs also to be emphasized that the swelling in acids is in no sense a main function of the concentration of the hydrogen ions. Gelatin, for example, swells more in the weakly dissociated acetic acid than in the practically completely dissociated sulphuric acid, while, on the other hand it is precipitated (that is to say, dehydrated) through picric acid which is another highly dissociated acid. Here as in other purely physico-chemical reactions it is not merely a matter of the hydrogen ion concentration but equally important or more important is the concentration of the *non-dissociated* acid molecules.

Inspection of an eye which has been permitted to swell in an acid shows the eye to be in a state which clinically we would call *glaucomatous.* The cornea is, moreover, steamy or opaque (Fig. 44). In the terms of colloid chemistry we deal with an increased water absorption by some of the ocular colloids while the clouding represents an acid coagulation of a second group of the biocolloids. In the case of this second group the acid concentrations employed do not bring about an increased but rather a decreased hydration and coagulation of the involved materials. Since our tissues represent a mixture of very different types of colloids, this double effect is readily intelligible colloid-chemically.

§26.

As also shown by MARTIN H. FISCHER, these combined swelling and coagulation processes reappear in many cases of *nephritis*.[1] The method of handling these cases therapeutically through the introduction of salt solutions — more particularly of solutions alkaline in nature — as has been done with great success since FISCHER'S experiments, is also based upon a colloid-chemical understanding of their effects. Such salts inhibit the swelling and coagulating effects of the acids formed in the pathologically affected tissues just as they decrease their effects upon simple mixtures of colloids in a test tube.

I can only mention in passing that *inflammation* has also been discussed from a colloid-chemical point of view,[2] that the unknown substance which is associated with goiter[3] is undoubtedly colloid in nature, that the immune reactions in their mutual adsorptions and precipitations offer a field full of unlimited possibilities for the applications of colloid chemistry, that the so-called "colloid reactions" of serum or cerebrospinal fluid with inorganic colloids of gold (LANGE'S reaction), berlin blue or mastic are indicative of the diagnostic applications which may be made of colloid chemistry, that promising beginnings of

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[1] See MARTIN H. FISCHER, Œdema and Nephritis, third edition, 648, New York, 1921; as well as Kolloidchem. Beihefte, **4,** 343 (1913).

[2] A. OSWALD, Zeitschr. f. exp. Pathol. u. Therapie, **8,** 226 (1910); a review is found in Koll.-Zeitschr., **9,** 251 (1911).

[3] See E. BIRCHER, Ergebnisse der Chirurgie u. Orthopädie, **5,** 133; Zeitschr. f. exper. Pathol., **9,** etc.

a colloid-chemical theory of narcosis have been made.[1] Furthermore, the colloid state of bile salts and of uric acid is of importance in unravelling the origin of gallstones and the concretions found in gout, while protein solutions are able to keep these materials in solution in concentrations much beyond their solubility in water (H. SCHADE, WO. PAULI, H. BECHHOLD); an adsorption therapy has developed in which various diseases are treated with adsorbents like charcoal, different earths, etc.; and colloid-chemical points of view have brought light into the nature of some of the processes observed in the healing of wounds.[2] You observe that one needs much breath merely to list the chapters in which colloid chemistry has already proved itself of service in medicine.

I would also point out that a whole series of inorganic colloids is now being used therapeutically — colloid sulphur in skin diseases, colloid mercury and mercurial salts in syphilis, colloid nickel in meningitis, colloid silver for the antiseptic treatment of wounds and in the management of infectious diseases like gonorrhea and ophthalmia. In ophthalmology colloid silver has almost completely displaced silver nitrate. It is of much interest that in comparative studies of the disinfecting action of different disinfectants colloid preparations of mercury have proved themselves of extraordinary activity even when used on many different types of bacteria. Colloid preparations of mercury according to the recent studies of H. FRIEDENTHAL seem to be the most powerful chemical disinfectants that we now possess.[3] But even the well known and important salvarsan is, in aqueous solution, in a colloid state, as I have long known from ultramicroscopic study and as has been

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[1] See S. LOEWE, Biochem. Zeitschr., **57**, 161 (1913), where references to the literature may be found.

[2] W. VON GAZA, Koll.-Zeitschr., **23**, 1 (1918).

[3] See G. STODEL, Les colloides en Biologie et en Therapeutique, Paris, 1908; a review appears in Koll.-Zeitschr., **4**, 321 (1909); H. FRIEDENTHAL, Biochem. Zeitschr., **94**, 47 (1919); R. EDER, Schweiz. Apoth. Ztg., Nos. 29–33 (1918) (a review lecture).

proved more recently by others.[1] Some years ago the interesting therapeutic applications of an inorganic sol, palladium hydroxid, were much discussed. It was used to combat obesity. Treatment consisted of the hypodermatic injection of the material into the fatty areas to be reduced, the injection being associated, it was said, not only with no unpleasant sensations but actually pleasant ones.[2] We have not heard of further progress along these lines but this is to be attributed, perhaps, to the war years which ✓ did away so largely with the material upon which the experiments could be made.

Of course — and I would like to emphasize this point in conclusion — the pendulum has perhaps swung too far in this application of colloid-chemical points of view to problems in materia medica and therapy. The advantage of colloid pharmaceutical preparations over others has perhaps been stressed too heavily; in England, for example, the claims have been carried to a point which not only seems nonsensical but one which must embitter any honest, no matter how enthusiastic, colloid chemist. Nor in the matter of theory does one need to go as far as J. Traube who represents perhaps the most extreme of the modern appliers of colloid-chemical points of view to practice.[3] But that aside from its chemical constitution, colloid-chemical factors like degree of dispersion and degree of solvation play an important part in the action of any pharmaceutical preparation — this is a view shared by even the most conservative workers in these fields and one to which, in good conscience, I too hold.

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[1] H. Bauer, Arb. Inst. f. exper. Therapie, Frankfurt, No. 8 (1919). See also A. Binz and collaborators, Ber. d. Dtsch. chem. Ges., **53**, 416 (1920).

[2] See M. Kauffmann, Münchener Medizin. Wochenschr., 525 (1913).

[3] The numerous papers of J. Traube are widely scattered. References to them and reviews may be found in the indices of the Kolloid-Zeitschrift; a recent paper dealing chiefly with the colloid chemistry of pharmaceutical preparations may be found in Biochem. Zeitschr., **98**, 177 (1919).

§27.

With this I must end the list of the applications which have been made of colloid chemistry to neighboring sciences. I do it with the hope that I may have convinced you of the inadequacy of any such lecture as today's to portray the countless applications that have thus been made or can still be made. I know that every one of you could, from the special fields of your particular endeavors, at once state a problem which might be investigated from a colloid-chemical point of view and which I have not at all touched upon. The day seems already here when no one speaker can by himself get even an approximately complete view of the whole field comprised under this heading of the applications of colloid chemistry to science.

V.

SOME TECHNICAL APPLICATIONS OF COLLOID CHEMISTRY.

FIFTH LECTURE.

SOME TECHNICAL APPLICATIONS OF COLLOID CHEMISTRY.

I shall in this last lecture survey the applications of colloid chemistry to some technical, industrial and practical problems. You might begin by asking whether there is any purpose in spending a whole hour in discussing these things. The concept of the colloids has become a familiar one only recently and so it might be concluded that the teachings of the colloid chemist find application in these practical fields only along narrow and specialized lines. Have enough and sufficiently important applications of colloid chemistry to technology really been made to justify spending a whole hour upon the subject? Let me in answer ask you to accompany me for a moment.

§1.

The clothes you wear, be they wool, cotton or silk, are animal or plant gels. They are dyed with colors which, in many instances, as the indigos and the blacks, are colloid in type. In the process of dyeing, adsorption and other colloid-chemical reactions take place between the colloid substrates of the fabric and the colloid dyes which color them. The leather of your shoes is an animal gel, closely related in its general properties to that prototype of the colloids, gelatin. Leather is tanned with substances of which the majority are colloids, and the whole process of tanning is punctuated with the colloid phenomena of hydration, dehydration and adsorption. The wood of the chairs in which you rest is made of cellulose, which in all its various forms is colloid in nature. The colloid swelling of wood, as I emphasized earlier, was used by the old Egyptians to aid their quarrying of stone. The woods of your chairs are held together by glue or with metals. You already know glue to be a colloid, but it may surprise you to learn that colloid chemistry has much to say in metallurgy and that steel, for instance, is a colloid solid solution. We shall return to this question. The paper upon which you write is essentially cellulose, in other words, again colloid. It has been given a body by being mixed with water-glass, with rosin or some similar material, in other words, with various colloids. The ink in your fountain pens is probably also colloid if it is the ordinary iron tannate, and colloid, too, is the hard rubber of your pen holders, prepared from that notoriously colloid mother substance, soft rubber.

I could continue this list indefinitely, pointing in this manner to one colloid after another in your immediate surroundings and belonging to the things of your every-day life. Perhaps you think — perhaps since yesterday's lecture you think you know — that I am possessed of a colloid mania because I see colloids everywhere. Let me admit that I do see colloids everywhere, only I do not believe that because of this I must be adjudged insane. It is simply a fact that *colloids constitute the most universal and the commonest of all the things we know.* We need only to look at the sky, at the earth, or at ourselves to discover colloids or substances closely allied to them. We begin the day with a colloid practice — that of washing — and we may end it with one in a bedtime drink of colloid tea or coffee. Even if you make it beer, you still consume colloid. I make these remarks in full earnest and with the request that if I do not prove my assertions to your satisfaction, you challenge me in the matter.

These facts leave no doubts in our minds as to the wealth and variety of the possible technical and practical applications of colloid chemistry. We only become conscious again of a great difficulty in making a proper choice of illustrations from the wealth of material before us.

To this difficulty come two others. Colloid chemistry as a systematically studied science is still very young. It cannot therefore be expected that any *conscious* application of colloid chemistry to technology has as yet been made in anything like the degree possible or probable. Many technical experts do not as yet even know that in their every-day practices they are working in colloids and that they should, in consequence, employ the fruits of scientific colloid chemistry in their various endeavors. This fact is often brought home to the colloid chemist who enters into discussion with practical men — something which, by the way, every scientist should do as often as possible.

I remember a conversation with a brick manufacturer who complained because two lots of clay which were alike chemically, yielded products of very different qualities. I expressed the conviction that a difference in the colloid state of the clays was probably responsible. "Colloid state, what do you mean by that?" he answered. Our conversation then turned to a discussion of colloids and he thus heard for the first time of the fundamental properties of materials in which he had worked for decades. Needless to add he became an enthusiast in colloid chemistry and I doubt not that he is now a regular subscriber to the *Kolloid-Zeitschrift.*

What I have said of the brick manufacturer is true of many other branches of industry. In many of them even that first of steps needs yet to be taken, namely, that of recognizing *the colloïd nature of the materials being worked upon and the colloid nature of the processes being used in manufacture.* The details of technical procedure need to be rewritten in the terms of colloid chemistry. Let it be clearly understood that this does not mean a mere restatement of facts and problems in different terms. When I say that rubber or cellulose is a solid colloid or that this or that technical process represents an adsorption phenomenon, I have to assume full responsibility for such statements and must be able to prove that the substances concerned show the fundamental properties of the colloid state or that the processes declared adsorptive in nature obey the adsorption laws. Such new definition in the terms of colloid chemistry is by no means always as simple as might at first appear. I beg you to remember this when in the following discussion I am often merely able to state that this is a technically interesting colloid as shown by such and such properties; that these processes are probably colloid-chemical in nature, etc. Complete colloid-chemical analysis and an accurate distinction between such processes in technological practice as are colloid-chemical in nature and such as are not has been found possible thus far in only isolated instances. There is a wealth of work to be done here, interesting not only from a scientific standpoint but from a practical one as well.

§2.

Permit me after this lengthy introduction to enter at once upon a consideration of the use of the inorganic colloids in practice. The whole list of elements finds use in colloid form in industry; to a few of these elements I would like to call your attention.

An interesting and characteristically American product consisting of an element in colloid form is the so-called Acheson graphite.[1] I have shown you this before under the name *aquadag* as a dispersion in an aqueous dispersion medium. I show it to you again dispersed in a mineral oil under the name *oildag*. These two preparations, which are much used as lubricants, prove on investigation to be typical colloids. This fact is revealed by ultramicroscopic examination, by the migration of the black phase in the electric field, by the precipitation effects produced through the addition of acids or sodium chlorid, etc. This

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[1] I am greatly indebted to Dr. Acheson for a large quantity of demonstration material.

technically important material serves also to illustrate my remark that much work is done with colloids without the workers being conscious that they are working with this type of material. Acheson did not begin with intent to prepare colloid graphite as is evident from his interesting addresses upon the history of his discovery. He only afterwards became conscious of the similarity and the relationships of his preparation to colloid types of materials.

Aside from the fact that aquadag, because of its black color and accessibility is useful as material upon which to demonstrate the fundamental properties of colloids (diffusion, dialysis, filtration, electrophoresis, coagulation, adsorption, etc.) it is a preparation which is of great colloid-chemical interest in other directions as well. First of all, its method of preparation is interesting, of which Acheson says that he finds it described in the Bible, or rather in the reports contained in the Bible of the methods employed by the Egyptians in the production of high-quality bricks. The Egyptians used straw infusions and other liquids rich in tannin in order to obtain uniform and finely divided clay. In the same fashion Acheson made use of commercial tannin preparations in order to obtain a highly dispersed, stabile and concentrated preparation of ground graphite. Just as when colloid gold is made with tannin, so in the preparation of colloid clays and of graphite, the tannins act as typical protective colloids. When graphite is ground in the presence of tannin the highly dispersed and colloid particles of graphite are encompassed as formed by the strongly hydrated tannin and so prevented from running together again into larger aggregates. But because of the great stability of the tannin toward electrolytes, it now becomes possible to evaporate a part of the dispersion medium until a graphite paste is obtained without the graphite settling out. The presence of this protective colloid also helps to keep the graphite finely divided when the lubricant in practice is exposed to the precipitation dangers incident to coming in contact with electrolytes.

Another point of interest is that the lubricating action of the graphite is intimately connected with its degree of dispersion. Even ordinary, coarsely dispersed graphite is a good lubricant, but its effectiveness is much increased by simple grinding, when the so-called *gredag* is obtained. But these coarse preparations are excelled by colloid graphite. We see here again a property, namely, lubricating activity, which increases steadily with increase in degree of dispersion. As the technologists among you well recognize, we still know very little regarding the properties which make a substance a good lubricant. Perhaps a closer study of this relationship between lubricating effect and degree of dispersion in heterogeneous lubricating materials may bring us some light, which may in its turn tell us what makes certain homogeneous liquids good lubricants and others not.

§3.

Other elements which are used in colloid form in technological processes are seen in the metals. An interesting and old application of colloid chemistry to technology is seen in the use of colloid metals for the production of *incandescent light filaments.* As you know, the lighting expert is constantly trying to bring the various light-giving bodies used in his lamps to as high a temperature as possible, since by this means he shifts the relation of the visible to the invisible, or heat rays toward the side of the light rays. For this reason the attempt is old which would replace the easily vaporized carbon filaments of our older lamps by the less volatile metallic filaments of tungsten, tantalum, etc. These metals have, however, the unwelcome property of great brittleness so that they can not be drawn into threads. To overcome the difficulty the metals were used in finely divided form. Colloid powders of the metals were made into pastes, often through the addition of some hydratable organic colloid, and the pastes were then squeezed through fine openings (as in the manufacture of artificial silk), and in this way very fine threads of the metals were obtained. I am able to show you here some hair-like threads of tungsten prepared in this manner (demonstration).[1]

Of special interest is the method of Kužel for the preparation of such colloid metals in powder or paste form. Prolonged grinding alone suffices to convert a low percent of the metal into the form of the colloidally divided powder. I show you some tungsten powder prepared in this way. Thrown upon a filter you observe that it runs through as soon as some distilled water is poured upon it (demonstration). This mechanical grinding takes much time and is very expensive. It is simpler and cheaper to make a colloid mud of the metal by the method of Kužel. In this the powdered metal is successively and repeatedly treated with acids and alkalies interspersed with washings in distilled water. The theory of the process is about as follows.

In a dilute acid the surface layer of the coarsely dispersed particles of metal goes into solution in finer form, yielding a smaller grain. This reduces a part of the powder to colloid dimensions. If the acid were allowed to act too long, the colloid thus formed would dissolve completely and disappear. The acid must therefore be neutralized and washed away, while the colloid which has been formed is separated by precipitation or filtration from the still coarsely divided material. By repeating the process, another part of the metal is brought into the colloid state, the whole procedure being repeated time after time until all the metal is gotten into colloid form.

We have however learned recently how to alloy the metals we are discussing with others and how through heat manipulation to get them into ductile form. As progress has been made along these lines, the more cumbersome colloid method discussed above has been displaced.

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[1] Colloid incandescent lamp filaments were kindly placed at my disposal by the Chemische Fabrik von Heyden.

§4.

Colloid metals and colloid metallic compounds are much used to give color to various materials. *Ruby glass* owes its red color to the presence of colloid gold. I show you three specimens which are "solid solutions" of gold in three very different and characteristic degrees of dispersion (demonstration).[1] The first is an almost clear and but slightly yellow mass of glass. This is obtained immediately after dissolving the solid gold salt in the glass. There is obtained in this way a molecularly dispersed solution of the gold in the glass, and one which, in consequence, is ultramicroscopically empty. The second preparation is the ordinary ruby glass in which the gold is contained in a colloid state. The third specimen is deep blue by transmitted light and orange brown by reflected light. The specimen is also distinctly turbid. It springs from a failure in glass manufacture in that, presumably through a too long heating of the glass, a coagulation of the red gold particles to the more coarsely dispersed blue particles has taken place — just such a change as I showed you in an aqueous dispersion medium when I coagulated the red gold (produced through reduction of gold chlorid by tannin) to blue gold through the addition of acid. These same facts as illustrated in the case of glass prove of what little importance is the kind of dispersion medium and how much depends upon the degree of dispersion in determining the variations in color in this substance.

Silver colloidally dispersed in glass makes it yellow or brown. Selenium colors it beautifully red or violet. The colloid metallic hydroxids also impart to glass some beautiful colors, as illustrated in the production artificially of the precious stones. The artificial rubies owe their color presumably to a colloid chromium, as do the artificial alexandrites, etc.

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[1] Different specimens of gold ruby glass were kindly placed at my disposal by Popper and Sons of New York.

§5.

An interesting illustration of color due to a colloid element is seen in the case of *ultramarine*. There still rages an old debate concerning the causes for the color in this mixture of different silicates, borates, etc., with sulphur or sulphur compounds. Even recently, nothing short of desperate efforts have been made to explain the color of this dye substance on the basis of its "chemical constitution." I say desperate because not only are the quantitative relationships found in the different ultramarines totally different, but on heating the normal ultramarine, uncolored, grey, yellow, red, blue and even green ultramarines can be produced, as shown in these specimens (demonstration). On the basis of differences in chemical constitution we would have to assume that each of these different colors represented a different chemical compound.

What we observe is entirely analogous to what we discussed previously when dealing with the photohaloids. We can produce blue and green solutions of sulphur by simply introducing this element into molten sodium chlorid, into a borax bead, into liquid ammonia, into hot organic liquids like glycerin or by simple reduction of a thiosulphate with phosphoric acid as I showed you in the second lecture.[1] These facts render it most improbable that ultramarine is blue because of the existence in it of a specific blue sulphur compound. We have therefore come to the conclusion that ultramarine represents a solid solution of highly dispersed sulphur. The degree of dispersion may oscillate between molecular and colloid dimensions,[2] and as this happens the different colors discussed above which

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[1] See Kolloidchem. Beih., **2,** 449 (1911); also P. P. von Weimarn, Koll.-Zeitschr., **20,** 278 (1917); R. Auerbach, Koll.-Zeitschr., **27,** 223 (1920).

[2] The assumption that we have to do with a solid solution of elementary sulphur in the case of the ultramarines was first made by J. Hoffmann [see, for example, Koll.-Zeitschr., **10,** 275 (1912)], but that we deal with solid solutions possessed of a colloid degree of dispersion or of one approximating these dimensions, seems first to have been expressed by me [Kolloidchem. Beih., **2,** 449 (1911); also Koll.-Zeitschr., **12,** 61 (1913)].

represent different degrees in the dispersion of the element sulphur are produced.

Of the many facts which confirm this view, I would like to emphasize the analogy between the production of ultramarine and the production of ruby glass, of blue rock salt, etc. In making ultramarine the necessary salts and the sulphur are melted together at a high temperature. This yields the greyish white or yellowish "mother of ultramarine." This product is then reheated, cooled and reheated again, just as in the case of ruby glass, until the requisite color is obtained. The original product is obviously a molecularly dispersed solution, the particles of which, through reheating, are permitted to condense to colloid dimensions. Support for the correctness of this view may be found in mineralogy. Mineralogists are familiar with a complex, sulphur-rich, silicate compound known as hauynite which appears in different colors ranging from colorless to green and blue. It has been shown[1] that the colorless varieties may be colored blue or green by heating them with sulphur in a closed tube, an experiment entirely analogous to the production of blue rock salt by heating this with metallic sodium.

There exist reasons for believing that in the colors of many of the so-called sulphur dyestuffs (dyes produced by melting together sulphur and different organic compounds in the presence of alkali[2]) we have also to do with similar solid solutions of highly dispersed sulphur. There certainly exists little hope of explaining their colors on the basis of chemical constitution.

Let me in passing emphasize that the alkali used in the preparation of either the inorganic or the organic sulphur

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[1] See Koll.-Zeitschr., **12**, 62 (1913); also NAUMANN-ZIRKEL, Lehrbuch der Mineralogie, 665.

[2] See O. LANGE, Die Schwefelfarbstoffe, ihre Herstellung usw., Leipzig, 1912, as well as the review of this volume in the Koll.-Zeitschr., cited in the previous footnote. See also W. ZÄNKER, Zeitschr. f. angew. Chem., **32**, 49, (1919).

systems tends to increase their degrees of dispersion. It has, in other words, a peptizing or stabilizing influence.

As you doubtless know already, many of the native gels are used directly as coloring substances. I need but mention the hydrated or burnt iron hydroxid gels (terra di siena, umber, yellow and red ochre, etc.).

§6.

Colloid chemistry finds many applications in *photography and the various graphic arts.* I have already touched upon the fact that many inks like the old iron tannate inks and india ink are colloid solutions. Printing inks are given their proper body by being mixed with colloids. Gelatin and other colloid mixtures are used in different kinds of color printing, etc. Not only does the colloid chemistry of the photohaloids play a great rôle in photography, but many other colloid-chemical processes are encountered in the manufacture of dry plates. This is illustrated in the "ripening" of the photosensitive emulsions until an optimal size of "granule" is obtained, and in the different methods employed for the developing, intensifying and printing of dry plates. To those of you who are interested in these subjects I suggest a perusal of the many contributions of LÜPPO-CRAMER, R. E. LIESEGANG and others.[1]

§7.

Of other fields in which colloid chemistry plays an important part I would emphasize those of *ceramics and the hydraulic cements.* The earths and clays are in great measure typical gels, consisting, as they do, so largely of aluminium silicate and iron hydroxid, admixed with organic colloids of the type of the humus acids. The plasticity of the ceramic clays is dependent in large part upon their colloid content; and their changes with time, the effects of added straw infusions, of treatment with ammonia,

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[1] See the literature cited in the first footnote on page 140.

etc., are all processes intended either to increase their absolute colloid content or to increase the peptization or hydration of this content.

The effect of alkalies upon ceramic clays is so great and plays so important a rôle in modern industry that it "has produced a revolution in ceramics," as one of the first authorities in this field has expressed it. Addition of alkalies tends to "liquefy" the clays. A stiff clay when treated with proper amounts of alkali loses its stiffness and changes to a liquid. On the other hand, dry clay mixed from the beginning with relatively small amounts of water, but containing some alkali, yields a fluid or semifluid mass. The technical importance of these findings resides in the fact that by such means much smaller amounts of water need to be used and so a faster drying of the clay moulds is obtained preparatory to firing. But in this fashion the much-feared cracking and deformation ordinarily incident to the first drying is also greatly reduced. These alkalinized clays can, moreover, be *poured* and in this manner large objects like bathtubs can be made much more easily than by the older moulding process.[1]

The explanation of how the alkali produces its effects is somewhat complicated; in it at least three to four different colloid-chemical processes overlap each other. The clay, an electro-negative colloid, is peptized by the addition of small but definite amounts of alkali. This puts it into a more highly dispersed state, an effect entirely similar to that observed when other negative colloids, like those of the metals, are treated in this manner. Second, a swelling is produced in the particles of aluminium silicate, a process which apparently attains its optimum at

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[1] A discussion of the literature and of the patents covering the use of alkalies in ceramics may be found in J. K. NEUBERT, Kolloidchem. Beih., **4,** 261 (1913). A review of modern advances in ceramics with special reference to colloid chemistry may be found in H. ARNOLD, Chem. Ztg., 413, 426, 439 (1918). The important paper of E. PODSZUS, Koll.-Zeitschr., **20,** 65 (1917) where references to his earlier studies may be found needs special emphasis.

a somewhat higher concentration of the alkali than that needed for peptization. To bring about this swelling effect, time is needed. Third, the alkali affects the organic colloids like tannin, humus acids, etc., constantly present under industrial circumstances. These substances are also peptized in low concentrations of the alkali, while larger amounts not only leach them out, but bring them into a molecularly dispersed condition. In this way they lose their importance as "protective" hydrated emulsoids. The three effects work side by side, so that when the element of time is also added a fairly complicated picture results. In short periods of time, peptization and increase in viscosity tend to nullify each other. It is usually held that the clays which on admixture with water take longest to settle out are also the most fluid, but this parallelism which is much used analytically may be lost as with more time the effect of the alkali brings about an increased swelling of the clay particles.[1]

§8.

The technically important process of setting, as observed in the hydraulic cements (cement and mortar), may be defined chemically as a reaction between calcium and silicic acid associated with a taking up of considerable amounts of water. These are the fundamental changes which occur in the setting of all the cements even though the materials that are mixed with the cements and mortars are for various practical purposes very different.

These fundamental changes of chemical combination with hydration may already be observed when calcium oxid and sand are mixed together as in ordinary mortar. In the case of Portland cement, the effects of admixture with calcium and iron hydroxid are superadded. It is not our problem to say how much justice there is in the various specific chemical assumptions which have been made to explain the

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[1] See the detailed discussion by JOH. K. NEUBERT cited in the previous footnote.

nature of these fundamental setting processes. It is widely believed that there comes into play a whole series of different and, in part, crystalline compounds (mono-, di-, tri-calcium silicate; alite, belite, celite, etc.). I would only emphasize that every exclusively chemical theory is unable to explain the physical accompaniments which are so characteristic of the setting process. Chemical reactions associated with hydration, like those observed in the mortars and cements, take place between many substances without the reaction mixture developing the characteristic physical properties observed in the mortars and cements. In the setting of mortar or cement there must take place certain special changes besides the chemical which are responsible for the physical peculiarities resulting from these reactions. Recent investigations have proved the existence of such and it has been found that we again deal with colloid-chemical processes.[1]

From microscopic study of the setting process, it was long known that when cement is mixed with water, numerous needle-like crystals begin to form around every cement particle, consisting, supposedly, of calcium mono-silicate, while larger and smaller hexagonal crystals, presumably tri-calcium aluminate and calcium hydrate, appear in the interstices. But there appears also a structure which, while noted before, has had a proper significance given it only recently. *There forms about every cement particle a gel of calcium silicate, the volume of which increases steadily during the process of setting until it fills not only the interstices between the crystalline needles but all those between the individual cement particles.* It is the formation of this gel which is undoubtedly the most important factor in the process of setting and which gives the solid cement its specific physical properties. The gel serves to bind together not only the

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[1] See especially W. Michaelis, Koll.-Zeitschr., **5**, 9 (1909); **7**, 320 (1910); S. Keisermann, Kolloidchem. Beih., **1**, 423 (1910), where references to the literature may be found; as well as numerous shorter papers by P. Rohland to be found in the Kolloid-Zeitschrift.

individual crystals surrounding a given cement particle, but also the crystals of neighboring particles. Cement particles with their crystals become imbedded in a common sheath of gelatinous substance (Fig. 45) and it is this fact which gives cement its solidity. Felting of the crystalline needles could by itself not explain this solidity. The cement tends to become progressively harder as more and more water is taken from the binding gel into the innermost layers of the cement particles themselves. The gel which we have been discussing can be stained by various dyes (like anthrapurpurin) and so be made to stand out from the rest of the cement. Perhaps you would like to see an ultramicroscopic picture of this setting process. I show you such in Fig. 46, in which you may see very distinctly the needle-like crystals protruding from the gel mass.

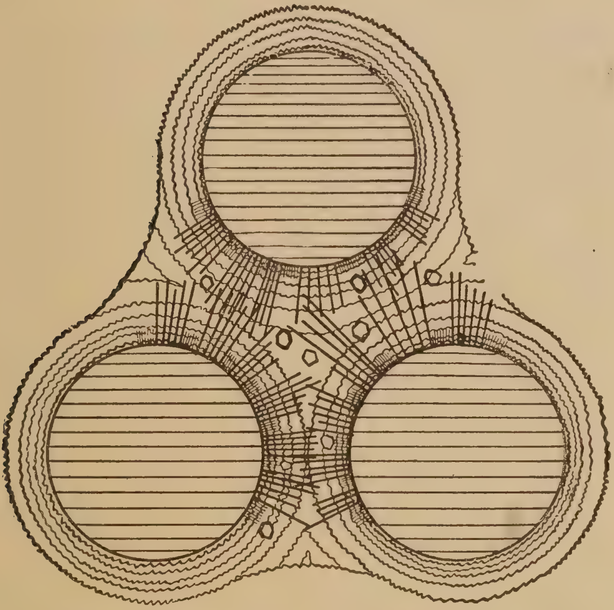

Fig. 45. — Diagram illustrating the changes incident to the setting of cement according to W. Michaelis. The serrated lines indicate the outlines of the gel.

If we accept the production of such a gel as the characteristic element in the process of setting, as has been especially well insisted upon by W. MICHAELIS, we at once obtain the explanation of a whole series of technological details. In order that the gel formation may be complete, there must, of course, be enough water present. It is for this reason that in testing for the maximal rigidity of cement samples, it is necessary to allow these to harden under water.

FIG. 46. — Ultramicroscopic photograph of cement in the process of setting, according to H. AMBRONN. Observe the delicate crystalline needles protruding from the gel envelopes.

Of especial technical importance is a regulation of the rate of the setting. Setting is retarded, for example, through the addition of such hydrophilic organic colloids as glue. This is explained colloid-chemically by finding that the glue takes up the water and then gradually yields the water to the silicate gel as this forms. Conversely, the setting process is hastened by adding organic acids like acetic acid. Colloid-chemically this means that acetic acid favors the formation of the silicate gel.

Entirely in agreement with this colloid-chemical theory of setting is the fact that so simple a process as the hydration of plaster-of-paris is also associated with colloid-chemical changes, according to the observations of A. Cavazzi, J. Traube, P. Wolski and myself.[1] A 3 to 4 percent suspension of plaster-of-paris shows, for example, a beautiful and regular increase in its viscosity with time; the process of setting can, in other words, be followed quantitatively in this way, as can the gelation of a typical emulsion colloid. Electrolytes favor or retard the process according to the Hofmeister ion series; while the addition of 2 percent glue retards the setting so markedly that there is no longer any change in the viscosity of the suspension with time.

§9.

I come next to an especially important chapter in technology, that of the application of colloid chemistry to *metallurgy*. I must preface my remarks by saying that the possibilities which colloid chemistry holds for the explanation of many metallurgical problems have hardly, as yet, been recognized. If in the following I venture some colloid-chemical points of view to explain various metallurgical questions and you find these not touched upon in your studies of the orthodox authorities who work in these fields, please know that I do this only because I am convinced that

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[1] Wolfgang Ostwald and P. Wolski, Koll.-Zeitschr., **27,** 78 (1920) where references to the older literature may be found.

the colloid-chemical or dispersoid-chemical point of view is going to have a remarkable future in metallurgy.

Problems which are definitely colloid-chemical in nature appear in the initial processes of mining. It is well known, for example, that gold can only with great difficulty be extracted from deposits which are rich in various earths or clays. The metal present in these materials is probably highly dispersed; but, more than this, it is probably held so fast or is so surrounded by the gelatinous hydroxids and silicates of aluminium and iron constituting these earths that the ordinary washing schemes do not suffice to extract the gold. The gold is "masked" by the hydrated colloids just as iron is masked through the presence of organic substances — in other words, the ordinary analytical reactions of the metal are not obtained until the organic parts have been destroyed. In order to make use of these minerals, it would be necessary to destroy the various inorganic colloids or to separate the metal from its adsorption complexes — a colloid-chemical problem which up to the present time has not been solved satisfactorily. Even relatively pure gold when colloidally dispersed is not taken up easily when shaken with mercury — a fact no doubt attributable to the difficulties incident to obtaining adequate contact between the colloid particles and the surface of the mercury.

The practice of *flotation* has recently assumed extraordinary prominence in mining. It will be simplest, perhaps, if I demonstrate an experiment in flotation in order to familiarize you with the fundamental principles which are at stake. I have in this mortar a mixture of white kaolin and some finely ground carbon. I could use graphite in place of the latter. When this mixture, which is to represent a ground-up ore, is shaken with water a grayish-black suspension is obtained in which the carbon or the graphite represents a valuable "ore" mixed in unpleasant and intimate fashion with the valueless kaolin representative of the "gangue." The technical problem at stake is this: how can we get the carbon or the graphite free from the kaolin? This end can be accomplished in simple and clean-cut fashion as follows. I add to the flask containing the gray suspension a few cubic centimeters of xylol, benzol or some other hydrocarbon not miscible with water — even kerosene will do — and shake a minute or two. An emulsion is formed but this soon creams and the hydrocarbon droplets run together. At the same time, however, — and this is the scientifically and technically interesting moment — *the hydrocarbon droplets take to the top with them the carbon or the graphite particles but not those of kaolin.* You see for yourselves how the carbon particles have formed a black layer at the top while the slightly gray kaolin, the "gangue," has settled to the bottom.[1] The separation we sought to accomplish is therefore made. Sulphid ores can in this fashion be separated from their accompanying gangue. As a matter of fact, ground up ores are often so treated as to convert their contained metals into sulphids in order that by flotation means they may be concentrated the more easily.

What now is the theory of this and similar technological procedures? I can answer this best by showing you another experiment. I have here six pieces of paper, each of an area of two to four square centimeters, cut from the advertising pages of an illustrated journal. Three of the pieces are white on both sides, that is to say, nothing is printed upon them. The other three have been printed upon on *one* side. I shake up the six leaflets in water until they have been freed from adhering air and have sunk to the bottom of the Erlenmeyer flask (demonstration). A few cubic centimeters of xylol are now added and the flask is again shaken for a moment. The coarse emulsion which forms, separates rapidly. The paper leaflets are now, however, no longer evenly distributed. The three white papers have sunk in the water but the three black ones

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[1] Details regarding this and other experiments in flotation may be found in Wolfgang Ostwald, Kleines Praktikum der Kolloidchemie, 110, Dresden, 1920.

float high in the surface between the water and the xylol with their black faces turned toward the xylol.[1] Why? Evidently because printer's ink ground up in oil is more easily *wetted* by xylol than by water and it takes work to tear the layer, printer's ink-xylol, in two. This is a measure of the force with which the paper adheres to the xylol. In similar fashion, carbon, graphite, sulphids, etc., are better wetted by hydrocarbons than by water wherefore they too "stick" better to the droplets of the former than to the latter and so rise with the hydrocarbon droplets in the "flotation" treatment of ores. This is, in brief, the explanation of its fundamental nature.

Another phenomenon in metallurgy, colloid-chemical in nature, is seen in the deposition of metals by electrolytic means. The structure of an electrolytically produced precipitate is markedly influenced, for instance, through the addition of traces of organic colloids like gelatin, albumin or dextrin. When present in certain definite concentrations, these colloids bring about a great increase in the degree of dispersion of the electrolytically produced precipitate. Instead of voluminous macro-crystalline or micro-crystalline precipitates, there are obtained dense, finely structured layers showing a smooth polish. The Germans call this "Glanzgalvanisation."[2] Colloid-chemically we may understand what happens by remembering that the added colloids are of the group of the hydrated emulsoids. As the presence of tannin or gelatin tends to produce gold in highly dispersed form, just so do the hydrated emulsoids act in the case of the electrolytic deposition of the metals — a process which also represents a condensation of highly dispersed particles to grosser ones. I can only mention in passing that the

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[1] The experiment goes well provided print paper which has been sized (with *glue*) is used. If ordinary unsized newsprint is employed, indefinite results are obtained because the oil from the printer's ink has soaked into all the paper and usually penetrated it.

[2] See, for example, E. Müller, Zeitschr. f. Elektrochemie, 317 (1906); a review is found in Koll.-Zeitschr., **1,** 60 (1906).

making of mirrors, like those of silver, represents an analogous dispersoid-chemical process.[1]

§10.

The most important applications of colloid and dispersoid chemistry are, however, to be found in the metallurgy of the *alloys* — more especially in the metallurgy of iron and steel. Because of the newness of the point of view and the importance of the subject, I beg you to let me enter into a few details.

As you know, the alloys, like the different steels and irons, show differences not only in chemical composition but in structure. You are all familiar, for example, with the coarse fracture of the ordinary cast iron as compared with the microscopic or even sub-microscopic structure of the finer grades of steel. You also know that even with constancy in chemical composition one and the same steel may show very different structures and that the nature of these structures is much influenced by variations in the temperatures to which the metal has been exposed, by the suddenness with which these temperature changes have been brought about, by tempering, by mechanical stresses and by simple ageing. It is possible, in other words, to obtain from one and the same mixture of iron and carbon a series of dispersoids showing different degrees of dispersion which may range from the type of the coarsely crystalline to that of the microscopically non-crystalline "solid" solution. We discover a series of dispersoids of iron and carbon (and the same is true of other alloys) entirely analogous to the series of dispersoids which I showed you in the case of sulphur, of sodium chlorid, of silicic acid, etc.

This simple and entirely familiar observation that two metals may be mixed into each other with the subdivided particles showing different degrees of dispersion, becomes

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[1] See V. Kohlschütter, Koll.-Zeitschr., **12**, 285 (1912); further papers are listed in the indices of the Kolloid-Zeitschrift from **12** on.

tremendously important in the light of our knowledge of the dispersed systems. *The technical and physico-chemical properties of an alloy are largely dependent upon the size of the subdivided particles constituting it.* Coarsely structured alloys are, as a rule, brittle and non-elastic, while in the words of the metallurgist, W. GÜRTLER, "a finely granular material and the absence of every marked or sharply defined structure are the signs of a mechanically valuable product."[1]

Even though this relation between degree of dispersion and technical properties has been generally recognized, it has by no means been regarded as of the importance which modern authors, among whom I should like to count myself, have assigned to it. Two other physico-chemical principles are still assumed to be of chief importance, the phase rule and VAN 'T HOFF's concept of the solid solution,[2] while the

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[1] See W. GÜRTLER, Handbuch der Metallographie, **1**, II, 450, Berlin, 1913.

[2] In spite of my great admiration for the progress that has been made in metallography through the introduction into this field of the concepts of chemical equilibrium, the phase rule and VAN'T HOFF's notion of solid solution, I cannot help emphasizing the need of caution in all this, for these concepts are all based upon the truth of certain assumptions. The concept of equilibrium, for example, assumes that we deal with states of equilibrium which under experimental conditions may be reached from either side. It is, however, characteristic of alloys (like the steels) that the changes taking place in them never come to a stop. The belief that true equilibria are attained in these solid mixtures therefore lacks support. It seems worthy of note that we find in the metallic world no reference to the fact that GIBBS' phase rule may be applied only if the conditions presupposed existent by the author of the rule are really present and since these are *not* satisfied in the majority of the alloys, application of the rule is therefore forbidden. GIBB's rule is valid only for equilibria in systems in which, to use the words of WILLARD GIBBS himself, the energies existent in the surfaces of the phases composing the system may be ignored. It is valid, in other words, only for macro-heterogeneous systems. These conditions are not fulfilled in the case of the dispersoid alloys, particularly not in those which are technically most important and in which the degree of dispersion is particularly high. GIBBS' phase rule cannot be applied to these alloys any more than it can be to ordinary liquid colloids. Metallurgy, moreover, confines itself to solid solutions in the sense of VAN'T HOFF, in other words, to molecularly dispersed solutions. It practically ignores, therefore, the question of degree of dispersion. The technically far more important *colloid*

relation between size of granule and physical properties has been regarded as of only secondary significance.

Numerous texts are, of course, available which deal with these obvious physical relationships, though their number is greatly exceeded by such as deal with the more purely chemical aspects of the problem. What has been lacking has been proper emphasis upon the tremendous importance of size of granules to physical properties and relative lack of importance of the specific chemical composition of the alloy. There was missing, to put it briefly, a proper correlation of the phenomena observable in these fields with the analogous phenomena observable in other fields and in which these relationships could be followed in simpler and more general fashion. This correlation is splendidly made when it is recognized that the problems of the physical chemistry of the alloys is that of the physical chemistry of the dispersed systems and of colloid chemistry. *For what is the study of the dispersed systems but that of the relation between size of granules and physico-chemical properties, and what is colloid chemistry but the science of a special subdivision in this realm?* And have we not found that changes in degree of dispersion constitute a factor which brings about incomparably more radical variations in the physico-chemical properties of any dispersoid than are observed, for instance, between the properties of different steels? Colloid chemistry has shown us that the physico-chemical properties of the dispersoid change with changes in the size of the dispersed granules and that these differences in degree of dispersion are the chief factors of moment, distinguishing the colloids in this way from the molecular solution on the one hand and the coarse suspension on the other, while at the same time serving to unite the two. From the teachings of colloid

solid solutions, to the wide distribution of which I called attention some twelve years ago [see, for example the article of P. P. von Weimarn, Koll.-Zeitschr., **7,** 35 (1910)], have to the present time received no conscious treatment in metallography excepting by C. Benedicks (references to whose work are given later).

chemistry, it cannot be gainsaid that in metallurgy, too, the relation between size of granule and properties belongs to the *most important* and *most widespread* of all the relationships with which we are familiar in modern physical chemistry.[1]

§11.

If we try to classify according to degree of dispersion the different structural elements which enter into the iron-carbon compounds, we may begin with the three metarals, iron or ferrite (with which may be included its various allotropic forms) iron carbid (cementite) and carbon. Carbon appears in the dispersoid series: graphite, tempering carbon, hardening carbon.

Graphite is a coarsely dispersed carbon; hardening carbon, an extraordinarily highly dispersed one. According to prevalent hypothesis, the carbon in this material is supposed to exist in molecular, solid solution. Tempering carbon occupies a middle position in the matter of degree of dispersion and physico-chemical properties. *The allotropy of these carbons is a dispersion allotropy.* The degree of dispersion in hardening carbon is, perhaps, not entirely molecular. It apparently occupies a transition point between colloidally and molecularly dispersed solid solutions. According to some of my still unpublished experiments, the so-called EGGERTZ solutions of this hardening carbon, as obtained by solution of steel in dilute nitric acid, are obviously colloid in nature. They scarcely dialyze, are ultramicroscopically heterogeneous, etc.

Iron carbid or cementite also presents different degrees of dispersion. Primary cementite is coarsely crystalline, segregated cementite somewhat finer, perlitic cementite finer

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[1] W. GÜRTLER in his admirable handbook lays more emphasis upon these important relations between the degree of dispersion and physico-chemical properties than any other author, though, to my mind, still not enough. See in this connection the paper of P. P. VON WEIMARN, Internat. Zeitschr. f. Metallographie, 65 (1911), as well as the remarks of W. GÜRTLER following this paper.

still. The finest of this series of materials may show so slight a structure that, in the words of W. Gürtler, it represents "an almost molecularly dispersed solid solution."

Even ferrite presents different degrees of dispersion, though the relationships here are complicated by the fact that iron by itself appears in a number of different forms which are allotropic in the ordinary sense of the word.

§12.

After these primary elements we need to consider the innumerable secondary ones which result from their combination. Of especial importance are mixtures of ferrite and carbon and of ferrite and cementite. From the many illustrations available, I touch upon a group which is interesting because of its importance in the technology of steel, and because it concerns a field which has been analyzed dispersoid-chemically by the Swedish investigator, C. Benedicks.[1] I refer to the series obtained when steel is chilled at different rates, namely, austenite, martensite, troostite, osmondite, sorbite and perlite. In this series austenite and martensite (perhaps, also, hardenite) are the most highly dispersed. They are probably molecularly dispersed mixtures obtained when the chilling is brought about very rapidly. Perlite is obtained with slower cooling. It shows[2]

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[1] C. Benedicks, Zeitschr. f. physikal. Chem., **52,** 6 (1905); Jour. Iron and Steel Inst., 352 (1905); Koll.-Zeitschr., **7,** 290 (1910). In studying the well-known text on siderology of H. von Jüptner, without being aware of the contributions of Benedicks, I arrived, in 1909, at a colloid-chemical view of metallographic processes, the theoretical and experimental results of which were published, in part, in some of the papers which I have cited. Not until later, after I had made a whole series of colloid-chemical experiments, as with the Eggertz' solutions, did I run across the short first paper of C. Benedicks, cited above, in which he expressed in very clear fashion a part of these colloid-chemical notions. It was after this that I wrote to C. Benedicks asking him to collect his views and to allow me to publish them in the Kolloid-Zeitschrift.

[2] Beautiful illustrations of perlite structure may be found in the article of C. Benedicks, Koll.-Zeitschr., **7,** 290 (1910). The structure reminds one strongly of Liesegang's rings.

characteristic lamella-like deposits of cementite which are easily visible microscopically and sometimes even macroscopically. Perlite is, in other words, a relatively coarse dispersoid. Between these extremes of martensite and perlite are found those which bridge the gap in perfectly smooth fashion, namely, troostite, osmondite and sorbite. It is for this reason that Benedicks came to the conclusion that these intermediates represent solid *colloid* solutions. *Troostite is evidently a colloid solution of cementite in ferrite; perlite is the coarsely dispersed or coagulated product of this cementite-ferrite sol.*

Faith in the existence of these colloid intermediates seems not only justified but absolutely necessary when it is remembered that *molecularly dispersed or coarsely dispersed metarals in moving from the one class into the other must pass through the colloid realm.* The only question at stake is whether it is possible to fix the material at the moment in which it is passing through this middle region.

But to this end solid dispersion media and the sensitiveness of alloys to external conditions obviously offer the best possible opportunities. Troostite is best produced through careful reheating of steels. This is no doubt because in this fashion a condensation is brought about of the previously molecularly dissolved carbon or cementite particles contained in the original martensite or austenite. The heating process and its results are, in other words, analogous to the repeatedly discussed conditions best designed to yield colloid solutions of gold, of sodium or of sulphur from their molecularly dispersed solid solutions. As known to everyone, carefully regulated increases and decreases in temperature are constantly used in the manufacture of metallic products to get these to show as fine a grain as possible.

But of especial importance are the relations which exist between these differently dispersed states[1] of the metarals

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[1] W. Gürtler (l.c.) has also repeatedly emphasized that not a definite chemical or physical property, but rather a definite structural state — in other words, a definite relationship of the differently dispersed metarals

and the technical and physico-chemical properties of the resulting metallic products. As emphasized by C. BENEDICKS, the efforts of the metallurgist are constantly directed toward the obtaining of a maximal elasticity and toughness of his technically important alloys. To accomplish this he tries, as far as possible, to get all the constituents of his alloys into a colloid degree of dispersion. As BENEDICKS puts it, "a correctly produced hair spring consists of troostite; the cry is always for steel rails consisting of sorbite; the tendons of technology, our steel cables, are, like the tendons of the human body, colloid in structure. The dispersion medium in all these instances is a distinctly crystalline body, the separate crystals of which man has for ages past tried to keep just as small as possible."

What is interesting in conjunction with these observations is that many of the most important technological properties of the metallic alloys attain their optimum in a region of medium or colloid degree of dispersion and not, for example, in a higher or molecular one. The property of hardness, for instance, grows steadily with increase in degree of dispersion, yet a suddenly cooled, "hard as glass," austenitic steel becomes so brittle that the progressive increase in hardness soon has a limit put upon it. Elasticity, toughness, modulus of rupture, rate of solution in dilute acids, coloration intensity of structure through iodin or picric acid, all these and many other properties attain their optimum in a region of medium grade of dispersion. Such facts regarding the alloys parallel the variations in color, opacity, viscosity, etc., which we discussed in our second lecture, where we also discovered that a medium or colloid degree of dispersion allowed these properties to appear in most

to each other — is characteristic of the technically important iron alloys, and that many of the names given to structural elements do not, as a matter of fact, refer to different individual structural elements, but cover their state of subdivision and of admixture with each other. Of the more recent papers see J. CZOCHRALSKI, Stahl und Eisen, **36,** 863 (1916); W. GÜRTLER, Zeitschr. f. Metallkunde, **11,** 61 (1919).

intense form. The curves expressive of the solution velocity of a series of alloys (martensite, osmondite, troostite, perlite), in which a maximum is observed in the middle, the curves which show that in cast iron there exists an optimum for the degree of dispersion of the graphite and that this corresponds with a maximum of carrying strain,[1] these are curves thoroughly familiar to every colloid chemist.

But other metallurgical phenomena find a parallel in colloid-chemical ones. Certain steels on cooling show a viscosity maximum somewhere below 1700° C. With falling temperature they do not become progressively more viscid as do normal liquids but exhibit a great increase in viscosity followed by a sudden decrease.[2] This is the same behavior which we encountered previously in the separation phenomena of hydrated emulsoids, of critical fluid mixtures, of crystalline liquids and of molten sulphur. The parallelism justifies the conclusion that in the case of the molten steels there also occurs at the temperatures under discussion a separation in highly dispersed or colloid form which with still greater lowering of temperature yields a coarsely dispersed system. It is possible that the so-called pseudoeuctectoid melts[3] are like these liquid steels. According to R. LORENZ it is possible to make colloid solutions in molten salts, the so-called "pyrosols."

A further analogy of metallurgical behavior to that of the colloids is seen in the fact that the melting point of ordinary grey iron, for example, is decidedly higher than its solidification point.[4] The same phenomenon may be observed in any gelatin gel. The explanation in both cases seems to be that during and after solidification, the particles grow to larger aggregates; and the melting point of large particles is decidedly higher than that of more highly dispersed ones.

It must also be pointed out that when the carbon content

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[1] See W. GÜRTLER, Handbuch, l.c., **1**, II, 308 (experiments of HEYN and LEYDE).

[2] See W. GÜRTLER, l.c., 131.

[3] See W. GÜRTLER, l.c., 188.

[4] See W. GÜRTLER, l.c., 186.

of a steel reaches a concentration of about 0.45 percent, a peculiar change in structure[1] takes place. While a so-called steel structure is characteristic of the higher carbon contents, there appears a so-called granular structure when the concentration of carbon is less. An analogous difference in structure characterizes, for instance, the setting of a concentrated and a dilute gelatin if this contains a little alcohol.[2]

I beg to conclude these remarks on the relation of colloid chemistry to metallurgy by pointing out that the phenomena of ageing, of fatigue and of distortion in alloys, whatever their kind, all tend in general toward a decrease in degree of dispersion — a behavior analogous, therefore, to that discussed previously as characteristic of these same phenomena in colloid systems. It is as true of a steel as of a colloid that the slightest alterations in external or internal conditions bring about great changes in its state. Things are no more at rest in a steel than in any colloid mixture.

§13.

This brings us to the important and varied applications which have been made of colloid chemistry to the organic industries and the technical arts. We are justified, as a matter of fact, in designating these as the colloid industries or the colloid-chemical arts.

To begin with the latter heading, we may take up, as of first importance, the processes of *dyeing and tanning.*[3] Of the many available illustrations I must again choose an

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[1] See W. Gürtler, l.c., 384.

[2] See, for example, Wolfgang Ostwald, Grundriss der Kolloidchemie, 1. Aufl., 350, Dresden, 1909.

[3] For a discussion of dyeing from a colloid-chemical point of view, see J. Pelet-Jolivet, Die Theorie des Färbeprozesses, Dresden, 1912, as well as his numerous papers in the Kolloid-Zeitschrift. Among newer studies in this field see those of R. Haller in the Kolloid-Zeitschrift and the Kolloidchemische Beihefte. For the colloid chemistry of tanning, see the reviews of E. Stiasny, Koll.-Zeitschr., **2**, 257 (1908) and Chr. Neuner, *ibid.*, **8**, 329 (1910); **9**, 65, 144 (1911). Numerous other papers upon these subjects by other authors especially W. Möller may be found in the Kolloid-Zeitschrift and in the Kolloidchemische Beihefte.

arbitrary few. In the first place, we must not in these fields make the mistake of considering everything we see as exclusively colloid-chemical in nature. Dyeing and tanning are complex procedures which aim at definite end results but they make no assumptions regarding the nature of the processes which are to lead to such results. A dyeing or tanning effect may be accomplished by very different methods, in the list of which appear many non-colloid-chemical ones. Some colloid-chemical processes must, of course, always appear as long as the material to be dyed or to be tanned is itself colloid in nature. In practice this is nearly always the case, for not only are textiles and hides typical gels or mixtures of such, but just as every chemical reaction into which a colloid component enters must in consequence show certain colloid-chemical peculiarities, just so must even the so-called "purely" chemical dyeing and tanning processes — as dyeing with an oxidizing agent or tanning with formaldehyde — show colloid-chemical peculiarities. But in many cases there is added to this colloid-chemical component resident in the substance itself that second one due to the fact that the dye bath or the tanning solution is colloid in nature. An unexpectedly large number of organic dyes as employed under factory conditions are colloidally dissolved and the same is true of nearly all the vegetable tanning materials, such as tannin and the different bark extracts. Many mineral substances as used in tanning are also colloid, as chromium hydroxid, sulphur, etc. In all these instances we therefore deal with reactions between at least two colloids, and to these is often added the effect of several more colloids. Thus in certain dyeing processes organic colloids like tannin or inorganic colloids like aluminium hydroxid are often added. In all such colloid reactions purely chemical ones come to play a decidedly minor rôle when compared with the adsorption effects and all their possible secondary reactions which we discussed in a previous lecture. As in the simpler examples of adsorption, we need in the adsorption of dyes and of tanning materials to recognize a whole series of different reactions as taking place side by side. In these there may predominate at one time electrical effects due to electrical differences between substrate and materials to be adsorbed, at another time surface tension effects, at a third, chemical ones. The literature abounds, therefore, in electrical, mechanical, chemical and other theories of dyeing and of tanning. These all tend to err in that they incline to place some one of these theories over and against some other; but as we found in our discussion of adsorption, the changes characteristic of this may be brought about in several totally different fashions, in which any one may be quite as important as any other.

Of great importance in dyeing is not only the accumulation of the dye in the material to be dyed, but its fixation in the material. The dye must be united in irreversible fashion to the fiber. The mistake is often made of alleging that adsorption alone cannot explain "fast" dyeing since, by definition, adsorption is always a reversible process. This view forgets that it all depends upon the intensity of the adsorption whether on rinsing in the pure dispersion medium some of the adsorbed material will again go back into solution or not. If the adsorption is so intense that practically all of the dye is taken out of the dye bath — and this is obviously the most economical method of dyeing — then none of the adsorbed dye is likely to pass out of the dyed material into the pure water, for this represents a still more dilute solution of the dye than did the almost decolorized dye bath which was in equilibrium with the concentration of the dye in the dyed textile. While adsorption alone may therefore lead to "fast" dyeing, secondary changes like polymerizations, secondary decompositions, direct chemical unions between fiber and dye, etc., often come about or are brought about to yield the ultimate "fast" result.[1]

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[1] See the main text for a discussion of secondary reactions consequent upon adsorption.

In similar fashion the process of tanning — the process, in other words, of changing hide into leather — can not be explained through mere adsorption of the tanning materials. The taking up of the tanning materials is only one part of the process though one which regulates as a rule all the further changes in state of the colloid substrate. If a colloid chemist is asked to say what constitutes the chief difference between hide and leather, he points out the following. Hide and leather are both structured gels; they are, in other words, collections of fibrils composed of collagen and other proteins arranged in that peculiar fashion determined originally by the anatomical structure of skin. In the untanned hide the fibrils are gummed together and contain much water. In leather they are more isolated and, at the same time, more strongly dehydrated or coagulated. If the more important stages of tanning are considered from this colloid-chemical point of view, it is clear that the initial swelling induced in the hide through immersion in acid (preferably an organic acid) amounts to this, that the individual fibers are "unravelled" as much as possible. The original gumming of the fibers, aggravated by any drying to which the hide may have been subjected is overcome. As a matter of fact, the cement substance holding the fibrils together may actually be hydrolyzed and thus brought into solution. This fluffing of the hide substance opens a path for the better entrance of the tanning materials and exposes a larger surface for adsorption. Complete tanning of a hide presupposes that the surface of every fibril will in this fashion be brought in contact with the tanning materials. But union with the tanning materials is also favored through such preliminary treatment just as mercerization (in other words, the fluffing of the cotton fibrils through previous swelling in alkalies) helps cotton to take up dyes. A second group of changes in state now takes place in hide. The fibrils are coagulated, that is to say, reduced to a coarser state of subdivision accompanied by a giving off of water. The trick of the tanner is the avoidance in this coagulation of a fresh felting of the isolated fibrils — this occurs frequently, for instance, in iron tanning. On the other hand the coagulation must not be carried so far that the fibrils lose all connection with each other and the leather be overtanned, in other words, be made brittle.

This colloid-chemical definition of tanning as *a limited swelling of the hide fibrils followed by their coagulation* holds also for the "physical" processes of tanning seen in *chamois tanning*. In this the fibers are also first isolated either through the mechanical manipulation incident to the introduction of oils and fats into the skin; or through the colloid-chemical effects produced by the oxidation products constantly present in the fats and oils used. Through the latter the fibrils are then subsequently also coagulated and dehydrated.

§14.

Industries which may in the true sense of the word be called colloid industries are seen in the group of those which work with cellulose. Pure cellulose is already a typical gel possessed of a beautiful ultramicroscopic structure; it shows typical swelling phenomena and on solution yields the highly viscid liquids which are characteristic of the hydrated emulsoids. It may be precipitated from these solutions through neutral salts or through dehydrating agents like alcohol.

These phenomena are all reversible. Of especial interest is a series which is irreversible in nature. I refer to the processes of parchment manufacture and of mercerization. Cellulose (in the form of filter paper or cotton, for example) swells in acids and alkalies of medium concentration more than in water, just as does gelatin or fibrin under similar circumstances. But following this treatment there occur various secondary changes which upon removal of the alkali and drying of the gel leave this in a much more highly dispersed and voluminous state than before. We have before us, then, parchment paper or mercerized cotton, either of which now shows new optical and mechanical properties to correspond with the colloid-chemical changes in state that it has suffered.

Various derivatives of cellulose and various combinations of cellulose with other materials in the form of solid solutions show typical colloid-chemical behavior. Best known are the cellulose gels used for the production of *artificial silks* and various *plastic masses*. Alkali-cellulose, like alkali gelatin, when treated with carbon bisulphid yields a remarkable substance known as viscose. From viscose is today prepared most of the artificial silk — an industry which already has an annual value of $200,000,000. Viscose shows all the characteristics of a hydrated emulsoid. The whole process of viscose silk manufacture is naturally honeycombed with colloid-chemical phenomena. The freshly prepared viscose is first aged or ripened before it yields a product optimal for spinning. The velocity of this internal change in state can be influenced through the addition of various substances. The originally fluid fibers must be coagulated; to accomplish this end the patent literature is filled with such a long series of different processes that it is safe to say that this coagulation phenomenon in viscose probably represents the best studied of the whole line of coagulations in emulsion colloids. These internal changes in state must, moreover, be inhibited at a certain time else the fiber becomes brittle. The tendency of the fiber to swell in water or steam and the consequent weakening of the fiber must be reduced to a minimum. The whole industry represents an unbroken succession of colloid-chemical processes.

Other cellulose compounds and solutions of them, like that of cellulose in ammoniated copper oxid, may be employed in similar fashion. Artificial silk can also be prepared from gelatin, though when this is used other methods of coagulation must be employed than in the case of viscose. Cellulose esters may be used to prepare transparent varnishes such as are employed upon aeroplanes, and these same materials are used for the production of plastic masses of various types.[1] The best known of these plastic masses is celluloid, that peculiar and scientifically little studied solid solution of cellulose and camphor, the uses of which are familiar to every one. Because of its high inflammability numerous cellulose derivatives such as cellon and acetyl cellulose ester have been introduced to take its place.

I should like to call your attention to some further plastic masses which are also colloid gels. Galalite is nothing but a casein, so treated that it no longer shows any powers of swelling. Bakelite is a condensation product derived from phenol in the presence of alkali and formaldehyde. It may be obtained in all states of aggregation varying from a soft, jelly-like material to a brittle, almost stony, resin-like mass. Bakelite is interesting colloid-chemically because it is a typical isocolloid, that is to say, a dispersoid in which the dispersed phase and the dispersion medium are polymers of each other. We shall shortly come upon another illustration of this group of materials.

§15.

The manufacture of *rubber*[2] represents another typical colloid industry. A number of colloid and dispersoid-chemical processes are observable even in the first preparation of crude rubber. Soft rubber comes from latex, which consists of a dispersion of tiny droplets of tenacious liquid in an albuminous serum. Just as in ordinary milk, it is probable that the protein surrounds the soft rubber globules as an adsorption membrane; in other words, as a so-called "haptogenic membrane." This protein seems to play a

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[1] Regarding the manufacture of plastic masses and of artificial textiles — especially such as are derived from cellulose — see the review of J. G. Beltzer, Koll.-Zeitschr., **8**, 177, 313 (1911).

[2] Nearly all the newer papers covering the manufacture of rubber from a colloid-chemical point of view may be found in the original in the Kolloid-Zeitschrift and the Kolloidchemische Beihefte under the names of Wolfgang Ostwald, F. W. Hinrichsen, B. Bysow, D. Spence, D. Ditmar, P. Schidrowitz, etc.

great rôle not only in the original coagulation of the latex, but also in giving to soft rubber its characteristic mechanical properties. The protein is apparently of the group of the globulins, for latex is commonly coagulated through the addition of carbonic acid or of distilled water, both of them typical coagulation procedures for the group of the globulins. In fact, all the various coagulation methods employed seem to be nothing but protein precipitation methods. Their proper employment seems to be a fundamentally important feature in the whole process of soft rubber preparation.[1]

Freshly prepared raw rubber shows a marked syneresis. It squeezes off a protein-rich serum. A proper separation of this material is of great importance, since it reduces the possibilities for bacterial growth.

Raw rubber swells tremendously in different organic solvents, as I have already shown you. Upon the application of heat, and through mechanical agitation, a large part of the soft rubber may be made to go into "solution." In this process the remnants of coagulated protein left in the soft rubber undoubtedly play an important part, since they serve to counteract the tendency of the swollen rubber particles to go into solution. These solutions of soft rubber behave like typical solvated emulsoids. They show great absolute viscosities, great relative increases with rise in the concentration of the colloid, phenomena of ageing, etc. All the observed phenomena are complicated through the presence of traces of the protein. Through the presence of such may apparently be explained the fact[2] that upon addition of acids there occurs a rapid decrease in the viscosity of soft rubber sols. This viscosity of the soft rubber is of great importance in determining the life of the solid rubber. It has been found that, as a rule, a relatively high viscosity yields a lively rubber; in fact, under certain circumstances this parallelism is a quantitative

[1] See also in this connection Koll.-Zeitschr., **13,** 324 (1913).

[2] D. Spence, Koll.-Zeitschr., **14,** Heft 6 (1914).

one in that the viscosity value parallels directly certain mechanical properties of the vulcanized product like its resistance to tear.[1]

Of great importance is the process of *vulcanization* — that series of important physico-chemical changes which occurs when soft rubber is heated with sulphur or sulphur compounds. At least three different types of changes are to be distinguished from each other in the process of vulcanization: first, the taking up of the sulphur or sulphur compounds; second, their fixation; third, the changes in state in the rubber following therefrom.

The nature of the first of these processes is still a matter of lively debate. Some maintain it to be a typical adsorption phenomenon, while this view is cast aside entirely by others. How greatly opinions differ is well illustrated in two papers which appeared almost simultaneously. In one of them the author took it almost for granted that a colloid like rubber should show adsorption phenomena; in the other, the author concluded that not a single fact argued for the importance of adsorption in the process of vulcanization. Since I was the first to defend the adsorption notion — though I did not by any means hold it to be an entirely "self-evident" one — I naturally incline to the view that the taking up of the sulphur is really an adsorption process. This view is supported not only by the fact that the process is governed by the adsorption law, but by the results of D. SPENCE's extraction experiments which show that the amount of sulphur adsorbed is inversely proportional to the reciprocal function of the free sulphur.[2] After the

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[1] See A. VON ROSSEM, Kolloidchem. Beihefte, **10,** 117 (1918).

[2] In spite of these corroborative findings by D. SPENCE himself, he still maintains in his recent papers that adsorption processes play no important rôle in the process of vulcanization. Some misunderstandings have served to complicate the discussion. A criticism of SPENCE's most recently expressed views is left for the future. C. HARRIES [Koll.-Zeitschr., **19,** 1 (1916); Untersuchungen über die natürlichen und künstlichen Kautschukarten, Berlin, 1919] has recently come to the conclusion that the taking up of sulphur by rubber is largely an adsorption phenomenon. A review of the various theories of vulcanization may be found in G. VAN ITERSEN, Kolloidchem. Beihefte, **12,** 252 (1920).

sulphur has been taken up by adsorption an important chemical union may take place. But there also occurs at this time an important change in the state of the rubber to which we shall return later.

Permit me to add a few words regarding "synthetic" rubber, this newest of the children of organic chemical industry. This material, as you know, is made by polymerizing isopren and related hydrocarbons. In the process of polymerization the isopren passes through the several states of a slightly viscid liquid to a stiffer one, to end in a hard, crumbly mass. It is between the two extremes that we obtain a product most like natural rubber. This product may be separated as a gelatinous mass from the monomeric mother substance through the addition of alcohol. The synthetic rubber obtained by these methods may be used as a class-room example of an isocolloid or isodispersoid. In the first stages of polymerization the dispersion medium consists of the monomeric mother substance in which float the polymerized particles; in the medium and higher concentrations there seems to occur a transformation which results in the monomeric component becoming the internal phase while the polymeric form surrounds it as a gelatinous structure.

The synthetic product does not, for the most part, possess the life or vulcanization possibilities of natural rubber. The attempt has therefore been made to overcome this defect by introducing protein and similar colloids into the artificial substance though not as yet with entirely satisfactory results.[1] Interest in synthetic rubber has recently

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[1] The lack of success following present day attempts to give to synthetic rubber the excellent qualities of the natural product or even better ones through the introduction of protein into the rubber would seem to depend upon the difficulties incident to such introduction in sufficiently dispersed form. This end might be attained more easily if the synthetic product were first made into an aqueous emulsion, in other words, were first made into an artificial latex — a procedure mimicking, for example, the newer methods used in the manufacture of the margarines in which an artificial milk is also first made and from which there is then produced the butter-like product. I know, however, from personal experiments and those of adepts in the field

subsided somewhat because of the great fall in price of the natural product. This defection is, I think, not merited. It seems to me that interest in artificial rubber does not today center in the possibility of finding a substitute for the natural product, but more in the possibility of making a decidedly better one. The situation is not unlike that obtaining in the case of the metallic alloys. We did not in this field rest content with the utilization merely of such metallic mixtures as nature furnished us. Only as we have treated these in various fashions or have added other materials to them have we obtained the "noble" alloys which now serve us. It seems to me as though what we lack in the manufacture of a satisfactory synthetic rubber is the presence in it of a second heterogeneous substance like protein, just as we need carbon present in iron to give us steel; in fact this analogy between rubber and steel seems to me to be more than a superficial one. From a synthetic "noble rubber" materials might be produced showing properties far superior to our present day ones produced from the "natural" product.

What is the nature of the colloid-chemical changes which mark the change from raw rubber to the vulcanized? Can they be regarded collectively from some such general point of view as can tanning? Whatever is said must be applicable, of course, to natural and to artificial rubber for both can be vulcanized even though the resultant products are not equally good. To the colloid chemist, synthetic and natural rubbers are *isocolloids*, in other words, gels in which the structural elements consist of polymerized molecules in association with simpler molecules of the same chemical composition, — polymeric particles, for example, dispersed in a phase of monomeric ones. Natural rubber is possessed of a second type of heterogeneity because of the dispersion within it of protein, resin, etc., in finely divided form.

The surface capable of adsorbing sulphur is represented

that it is not an easy matter to make highly dispersed, stabile emulsions of rubber in an aqueous dispersion medium.

by the surfaces of the original latex droplets. Just as in the case of the fibrils in hide, these droplets are originally gummed together and must first be "loosened up"[1] either through heat (in the process of hot vulcanization) or through some substance which brings about their swelling (in the process of cold vulcanization). In either case the actual vulcanization, that is to say, the process of taking up sulphur seems to displace the equilibrium existent between the elements in the rubber, with their different degrees of polymerization, in the direction of *an increase in the more highly polymerized fractions.* Were a mass of rubber thought of as a series of fused latex droplets but with the outside of the mass more highly polymerized than the more liquid inside, vulcanization would represent a progressive solidification of the sphere. Whether the polymerization is thought of chemically or colloid-chemically (as for example a coalescence of particles similar to the "condensation" observed when a rubber sol is precipitated with sulphur monochlorid) is a question of secondary importance. The process of vulcanization, as the process of tanning, can also be carried too far, — and the rubber be made brittle. Vulcanization is therefore not unlike tanning, only in the case of rubber it is an isocolloid which is coagulated. Instead of being dehydrated the particles of rubber suffer a colloid-chemical condensation, in other words, the number of coarsely dispersed particles with their higher viscosities is increased. But, just as in tanning, a definite structure possessed by the gel as a whole must not be destroyed. Loss of such, as induced through too violent milling, may take all the "life" out of rubber.[2]

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[1] The lack of well developed internal "adsorption surfaces" may be to blame for the difficulties incident to the vulcanization of synthetic rubber, another fact which emphasizes the advisability of trying again to bring synthetic rubber into the latex state, or of vulcanizing it after it has gone through such.

[2] Space does not permit me to discuss the bearing of this colloid-chemical concept of vulcanization upon the related views of S. Axelrod, G. Bernstein, F. Kirchhof, C. Harries and others. I can only point out that

A word is necessary regarding vulcanization by exposure to radiant energy like ultra-violet light.[1] This procedure also shows many analogies to the physical phenomena seen, for example, in the coagulation of proteins and to the chemical ones observed in the photo-polymerization of styrol to metastyrol.[2] Mention needs also to be made of vulcanization "without sulphur," as when PbO or trinitrobenzene (Ostromyslensky) are used. Raw rubber can in these ways also be changed to a vulcanized product though its technical value is still low.[3] It would indeed be strange colloid-chemically if sulphur alone could coagulate rubber in the manner sketched above. It is more probable that the future will bring us as various a series of methods of vulcanization as we have today of tanning.

A word, too, regarding the so-called vulcanization accelerators, — materials which in the past few years have been much discussed and assumed considerable technological significance! These materials are, for the most part, neutral or basic nitrogenous compounds like di-methylanilin or hexamethylentetramin. The addition of a few percent of these substances not only shortens the time

the view is not universally tenable that vulcanization represents a "depolymerization" followed by a "polymerization." It is hard to imagine how such antagonistic effects can be produced when the external conditions remain the same, depending only upon the lengths of time that the rubber is acted upon. The concept sketched above is more specific in that heat and the swelling medium are supposed to produce a depolymerizing action only upon the cement substance existent between the original latex droplets or, expressed more accurately, only upon the surfaces of these structural elements. Once the surfaces are thus exposed, the sulphur can be adsorbed producing an opposite, namely, a polymerizing effect. In harmony with this concept is the observation of D. Spence, among others, that milled and unmilled rubber bind the same amount of sulphur in spite of the great mechanical differences observable in the products. Extremes excepted, milling can not expose more adsorption surface than can heating but the mechanical properties of the vulcanized product can be influenced just as the mechanical properties of a gelatin gel are changed when this is worked through a sieve and then pressed together again.

[1] See G. Bernstein, Koll.-Zeitschr., **11,** 185 (1912); **12,** 193, 273 (1913).

[2] See the dissertation of G. Posnjak, Das Metastyrol, Leipzig, 1910.

[3] See, for example, B. E. Bunschoten, Koll.-Zeitschr.. **23,** 25 (1918).

necessary for vulcanization by three-fourths but improves the mechanical properties of the product and its keeping qualities. It is well known that our German synthetic rubber could be made into useful products during the war only through the addition of these substances. Not so well known is the fact that my brother, WALTHER OSTWALD, and I were the first (in 1908) to recommend their use and to patent the process.[1] How these substances act colloid-chemically (aside from their chemical effects of retarding oxidation) whether, for example, they have a depolymerizing action like heat and materials which bring about swelling or whether they act as coagulants, is still an open question.

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[1] German patents 221310 (Nov. 1, 1908) and 243346 (Dec. 1, 1909). They cover particularly the addition of nitrogenous compounds to increase its lasting qualities. G. D. KRATZ [Jour. Ind. Eng. Chem., **12,** 318 (1920)] expresses surprise that "the two Ostwalds failed to note" the accelerating action exerted by these substances. Since the story of these patents may serve as a warning to others who make "scientific" discoveries, it may be well to tell it. The idea of stabilizing rubber and protecting it against depolymerization, oxidation, etc., was the outgrowth of biochemical experiments on the suppression of autoxidation. Laboratory experiments showed rubber to behave as expected. But as we did not have at our disposal the facilities for working out our experiments on a technical scale, the best known of the Berlin "rubber" laboratories was asked to test out the matter. This group of "experts" on the basis of their experimental studies concluded that the procedure had no practical usefulness. *Following this verdict* we foolishly dropped the patents already granted us. But we have had the satisfaction of seeing proof in the extraordinary development of this subject since, that we thought and observed correctly fourteen years ago.

D. SPENCE [La Caoutschouc, **17,** 10427 (1920)] in discussing the history of this subject states that he used organic substances, such as piperidin, in 1910, in other words, two years before the idea was patented by the Farbenfabriken, vormals FRIEDRICH BAYER. This may be, but that date is still two years after that of our patents. The statement that the Diamond Rubber Company produced large amounts of piperidin in 1909 may also be true, but even this is a year after our patents were granted. It would, moreover, have to be proved that the piperidin was not used in such "large amounts" merely for the recovery of rubber from vulcanized materials as per the American patent 805903 of 1905 (regeneration of rubber with pyridin bases).

§16.

The manufacture of *soap*[1] is another colloid industry. Through their viscosity, their powers of gelation and of swelling, the salts of the fatty acids again show themselves to be typical emulsoids. Of particular interest to the colloid chemist are the technical processes involved in the salting out of the soaps. Upon the addition of sodium chlorid, for example, to the boiled soap solution there follows a separation into two liquid layers, one containing much soap and little water, the other (besides glycerin) much water and little soap. This coagulation phenomenon as carried out in practice is one of the most typical and probably the most gigantic example that nature offers of the precipitation of a hydrated emulsoid. The phenomenon proves on a huge scale that in all emulsoids two liquid phases are really divided into each other.

The colloid chemistry of the soaps has recently been studied in systematic fashion by Martin H. Fischer. He has written a whole book from a colloid-chemical point of view on these technically important systems showing not only how the technical processes of soap manufacture may thus be furthered but, conversely, how the colloid chemistry of the proteins and the concepts of colloid chemistry itself may be clarified and developed through such study.[2]

I can only mention in passing that in the process of washing, colloid-chemical processes of all kinds, more particularly adsorption phenomena, play a great rôle.[3]

The manufacture of *starch*, of *glue*, of *mucilage* and of

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[1] See especially the reviews of F. Goldschmidt, Koll.-Zeitschr., **2,** 193, 227, 287 (1908); **5,** 81 (1909); **8,** 39 (1910); J. Leimdörfer, Kolloidchem. Beih., **2,** 343 (1911). Numerous other papers and references to such appear in the Kolloid-Zeitschrift.

[2] Martin H. Fischer, Soaps and Proteins, New York, 1921. A German translation by J. Matula is appearing in the Kolloidchemische Beihefte and in book form from the press of Theodor Steinkopff, Dresden.

[3] See especially W. Spring, Koll.-Zeitschr., **4,** 161 (1910); **6,** 11, 101, 164 (1911).

sizes of various kinds is also punctuated with colloid-chemical problems. The whole process of starch manufacture consists of nothing but the separation of particles of one size, the starch granules, from more coarsely dispersed ones, on the one hand, and from more finely divided nitrogen-containing colloids, molecularly dispersed salts, etc., on the other.

§17.

The colloid chemistry of the *foods* covers a field which we tread many times daily. I ask your pardon if I go into some detail.[1]

Everyone thinks that he knows something about food and so far as the phenomena of the subject are concerned, he does. And yet K. von VOIT and JUSTUS von LIEBIG bemoaned the fact in their day that there existed no real science of food. THEODOR PAUL has recently made the same lament.[2] Scientific study of the field still contents itself with chapters on analysis and the recognition of adulterants but chapters dealing with the preparation of food are hardly started. Much as everyone would like to obtain better food for less money, study of such questions is regarded as menial and best left to the cook. A scientific study of the preparation of food is considered as only amusing even in scientific circles. Many laboratories exist for the study of the products of human metabolism but there is only one institute in Germany for the study of food preparation and that was established during the war.

It seems to me that the chapters which are missing from our present volumes on food chemistry are those *in which colloid chemistry plays a chief rôle* — a view which is not mine alone. The following words may serve to illustrate what I mean. Because of the wealth of subjects available for discussion a choice has to be made and I shall, therefore,

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[1] I am using a lecture printed in abbreviated form in Chemiker Zeitung, No. 143 (1919).

[2] TH. PAUL, Biochem. Zeitschr., **93,** 365 (1919).

touch only upon the colloid chemistry of three important foods, — milk, bread and meat.

The chemist describes *milk* as a mixture of fat, proteins, sugar, salts and dissolved gases in much water. How would the colloid chemist do it? He would ask, first, regarding the state of subdivision of the different substances. For him milk is a polydispersoid, that is to say, a mixture of substances possessed of different degrees of dispersion in one and the same dispersion medium, water. As G. Wiegner has pointed out, milk contains all of the three grades characteristic of the dispersoids. The fat droplets, for the most part of microscopic size, are coarsely dispersed; the proteins such as casein, lactalbumin, etc., are colloidally subdivided; the milk sugar and salts are maximally dispersed, in other words molecularly or ionically. The coarsely dispersed fat is present in non-solvated form; the colloid proteins in a swelled or hydrated state. The colloid chemist, obviously, is interested in properties quite different from those which concern the analytical chemist. Does the colloid chemist's point of view represent anything more than a mere listing of some adventitious, unimportant properties of milk? As a matter of fact he can draw from his characterization of milk as a polydispersoid some not unimportant conclusions. Materials divided to a point approximating the colloid state change their properties with ease and so vary much when exposed to slight changes in their surroundings. The colloid chemist will therefore divide milk, from a theoretical point of view, into two fractions; into one which is relatively unstabile and which includes the colloids and the more coarsely dispersed parts of the system and into a second, which is relatively stabile and includes the molecularly and ionically dispersed portions of milk. Experience justifies this classification. While the content of electrolytes in milk as measured by freezing point determinations, for example, is fairly constant, the fat and the protein fractions vary greatly even in the milk of a single animal. We shall take up the qualitative variations in the fat and proteins immediately. From a quantitative point of view the importance of distinguishing between the two fractions is emphasized in the important law of CORNALBA and WIEGNER,[1] according to which the content of any constituent of milk is the more constant the higher its degree of dispersion. This fact is of importance when the question of the adulteration of milk through the addition of water is up. Trustworthy determination of such adulteration is by no means easy for the percentage of fat can not be relied upon because of its normal variations. For this reason the calcium chlorid test has steadily grown in favor. Upon what does it depend? It divides milk in practice into the same two fractions into which we have just divided it theoretically. The variable fractions (fat and protein) are separated and thrown away, the stabile fraction, the serum, being used for the test. Only when this stabile fraction shows definite variations from the normal may it be said with certainty that water has been added to the milk.

Let us now look at the unstabile fraction. It must first be recalled that the fat droplets in the milk of different animals differ greatly in size being finest in human milk. The importance of this fact for its digestibility is recognized both practically and theoretically. According to WENZEL's law, so important in colloid chemistry, the rate of a chemical reaction depends upon the extent of the reacting surfaces. The fat droplets of cow's milk may be made smaller by artificial means. Milk thus "homogenized" is markedly altered in its properties. Not only does it no longer cream spontaneously but the butter fat can no longer be removed from it by centrifuging; its internal friction is increased, etc., etc.

Similar variation in degree of dispersion and degree of hydration (swelling) may be observed in the purely colloid

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[1] See, for example, G. WIEGNER, Zeitschr. f. Untersuch. d. Nähr.- und Genussmittel, **27,** 425 (1914) where may be found references to his older studies.

portions of milk, particularly the casein. Human milk again shows the most finely divided casein particles; sheep's milk particularly coarse ones. When milk is heated the particles are increased in size. Acids, bases and even sodium chlorid bring about similar increases with changes in the degree of swelling as may be determined by microscopic or viscosimetric means.

Adsorption phenomena also appear in milk. We have defined adsorption as the concentration of materials in a surface. It is to such concentration that the films formed in milk owe their origin. That which forms when milk is heated is familiar to you. To such may be attributed the easy "boiling over" of milk. But adsorption phenomena may appear in the surfaces existent within the milk. Such surfaces are found, for example, wherever fat droplets touch the remaining portions of the milk. The formation of "adsorption films" about the fat droplets is therefore expected by the colloid chemist for he knows that protein solutions may be rendered protein-free by being shaken with mineral oils. The old dairy question regarding the physical state of these adsorption envelopes is answered by saying that they are gels and as such show the properties of both solids and liquids. Their presence has much to do with the making of butter and they are responsible, too, for the fact that the fat can be extracted only slowly and incompletely from milk when shaken with ether.

The uniformity of mixture in milk may be further disturbed by sedimentation or creaming. Specifically heavier particles sink while lighter ones, like butter fat, rise to the top. The velocity of such creaming is also dependent upon the colloid-chemical factors of degree of dispersion, degree of hydration, viscosity of the medium, etc.

Let us next consider the coagulation of milk. By coagulation of a dispersed material we mean reduction in the degree of its subdivision, a change often accompanied by destruction of the uniform structure of the system. Both the coarsely dispersed fat phase and the colloidally dispersed protein phase of milk may be coagulated. When the fat droplets run together the milk has buttered; when the colloid casein particles unite, the milk has curdled. In order that coagulation of the fat droplets may occur, the gel structure of their adsorption envelopes must be modified or destroyed. This is induced, as you know, by allowing a definite, medium degree of acid production to come to pass in milk or cream. The degree of swelling or the degree of dispersion of the proteins constituting the adsorption envelopes must be changed in order that the fat droplets will run together. W. Kirchner emphasizes the first in his textbook on dairying; W. Fleischmann the second, in his. To the colloid chemist both factors are probably of importance for the two tend constantly to appear together in colloids of the type here under discussion. The fact that the rate at which butter forms and that the quality of the butter are determined by the concentration and size of the fat droplets, by the acidity and the temperature, — all these things have their analogies in the fields of pure colloid chemistry.

The physical state of the clot when milk is coagulated has great importance. It is different when milk coagulates spontaneously from when coagulated through the addition of acid or rennin. When cheese is to be made it is required that the casein gel shall have a definite solidity, on the one hand, and yet a definite plasticity on the other, otherwise a right development and distribution of the gas bubbles may not occur and so the "holes" be not right, as in Swiss cheese, for example. Proper measurement of such mechanical properties belongs to the interesting field of gel physics.

When casein is coagulated by an acid or, better, by rennin, the whole system goes solid but the process does not stop there. The gel contracts and squeezes off a greenish-yellow "whey." Obviously, this is nothing but a vivid example of syneresis.

The colloid chemist can apply his science to many problems in *bread* making. In his terms, flour is made up of three dry hydrogels, plant protein, starch and cellulose. The coarsely dispersed powder contains salts, sugar, acids and water in molecularly dispersed form. Dough is a gel which colloid-chemically has a structure similar to milk, containing in molecularly dispersed form besides dextrin, sugar and alcohol, various salts, acids and gases; in colloid form, the "dissolved" plant proteins; in coarsely dispersed form, the swollen starch granules, gas bubbles, yeasts, lactic acid bacteria, etc.

It has the properties of both liquids and solids. Like any liquid it assumes the shape of its container even though slowly and gas bubbles arising in the mass take on a spherical or lens-shaped form. On the other hand, it can be cut in pieces like a solid body and if suddenly subjected to pull, it tears exposing irregular surfaces. Such combination of liquid with solid properties is characteristic of gels and solvated emulsoids.

What happens when bread is baked? Chemically, baked bread is not unlike dough, but colloid-chemically the difference is great. When baked the coarsely dispersed starch granules become highly dispersed and highly hydrated. The colloid albumins, on the other hand, are coagulated. Of great importance is the behavior of the gases produced when dough rises or is baked. In the process of baking the bubbles must not coalesce into large ones but must be fixed in a still finely divided state, just as solid reaction products may be kept in a state of high dispersion through the presence of a protective colloid. Only in this way will we obtain the coherent sponge of hydrated starch and coagulated protein permeated by innumerable small gas chambers which characterizes well baked bread. When the gas bubbles form too rapidly or come out in too gross form, holes or cracks appear in the bread thus giving rise to the commonest of baking failures. Well-made bread is a gel sponge or foam, analogous in its dispersoid-chemical structure to pumice or whipped cream, the mechanical properties of the bread gel standing about half way between these extremes.

The properties of flour which make it yield a good bread are known as its baking qualities. They are much discussed in practice for we seem to have no laboratory method of telling us whether a flour will bake well or not. In order to discover this a sample loaf must still be baked. As in the days of the ancients we do not discover metal in stones by chemical analysis but by fusing them. Can colloid chemistry help us in this flour problem, for it seems proved[1] that physico-chemical differences in the several constituents of flour are responsible for its baking qualities? As in other colloid industries (as those of rubber and artificial silk) it has been found[2] that the viscosity of a diluted flour gel parallels the physico-chemical properties of the concentrated gel. In keeping with the fact that the highly milled flour of war times yielded a poorer, heavier bread than the less milled flour of peace times, the viscosities of their "solutions" are also markedly different. The different baking values of wheat and rye flours are paralleled by corresponding viscosity differences. A medium concentration of acid in the dough is best for baking purposes and what this is may also be discovered by viscosimetric means. Flours which bake poorly are those which have a low "viscosity number." How sensitive is the method may be seen from the fact that hard or soft waters which influence markedly the baking qualities of a flour betray themselves in viscosimetric tests.

The "going stale" of bread is a familiar change which has not as yet been satisfactorily explained. It is most marked in white bread which becomes crumbly. The change is not due to mere water loss. Even in a tin box, in a sealed glass tube, in an atmosphere saturated with water vapor, bread goes stale. Chemical differences can not be dis-

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[1] See, for example, M. P. Neumann, Brot u. Brotgetreide, 284, Berlin, 1914; A. Maurizio, Nahrungsmittel aus Getreide, **1**, Berlin, 1917.

[2] See the papers of Wolfgang Ostwald and H. Lüers on the colloid chemistry of bread in the Kolloid-Zeitschrift for 1919 and 1920.

covered between fresh and stale bread. The colloid chemist, however, notes marked differences in swelling capacity and observes that the starch constituent is the fraction particularly affected. The process is at least partially reversible for when bread is warmed over its freshness may be restored. Furthermore, bread goes stale faster at 0° C. than at higher or lower temperatures. Taken all together the change has much in common with that observed when milk is coagulated and separates into clot and whey. Such syneresis may be seen even in ordinary starch paste. What must be the consequence of the syneresis? The sponge constituting the bread must suffer tension and its weaker lamellæ be torn. This is why the bread becomes crumbly. The squeezing off of the fluid is best seen in the first periods of going stale. Bread has then a moist feel not limited to the dextrin-rich crust but discoverable in the body of the bread. Colloid chemistry seems capable therefore of contributing to an understanding of this old and interesting problem also.[1]

Let us now consider *meat*. Histologically, lean meat consists of muscle fibers and connective tissue, biochemically of muscle proteins and collagen. The muscle proteins are typical colloids and collagen is not only the source of gelatin but its Greek root, κολλα, is the baptismal source of the whole science of colloid chemistry. Fresh meat is notably tough and difficult of digestion. Only after it has been "hung" does it become tender and less difficult of digestion. What are the changes which the meat has suffered? Shortly after an animal has been killed, its fleshy portions — the muscles — go into "rigor mortis" which, some twenty-four hours later, passes off. Only then does meat assume that degree of tenderness, juiciness and palatability which we cherish.

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[1] The papers of J. R. KATZ [Zeitschr. f. Elektrochem., **19,** 663 (1913); Zeitschr. f. physiol. Chem., **95,** 104 (1915); **96,** 288, 314 (1916)] should receive special mention. KATZ however attributes the going stale of bread to more complicated circumstances and uses colloid-chemical concepts like that of syneresis not at all or only as factors of secondary importance.

The onset and disappearance of rigor mortis are dependent upon a series of colloid-chemical changes in the muscle colloids. Shortly after death, various acids are formed in the muscle, particularly lactic acid. These make the fibrils of the muscle swell, the swelling expressing itself in that contraction of the muscle which characterizes the death rigor. Some authors, like O. von FÜRTH and E. LENK, believe that the acids are also responsible for the secondary softening of the muscle acting this time upon another colloid, myosin. This they suppose to coagulate later than the muscle fibrils or at a higher concentration of the acid. I think it not impossible that the relaxation of the muscle — an internal shrinkage — may also be but another illustration of that spontaneous change so often discussed as syneresis. The various theories[1] cannot be discussed further but it must be apparent that colloid-chemical ways — too many perhaps — of explaining these important practical questions are at hand.

The meats of different animals can be distinguished from each other by the amounts they swell in dilute salt solutions and it can also be determined in this way whether the meat has been freshly killed or hung, whether it has been frozen or dried, etc. Swelling capacity and degree of digestibility largely parallel each other. Veal, for instance, is not only easily digested but swells greatly. According to G. JUNG meat retains a greater water absorption capacity when salted dry than when pickled in brine. Pork can be distinguished from other meats by the fact that its water holding capacity suffers the least amount of change when cooked or dried. The effect of sour milk or vinegar upon meat, as in the preparation of "Sauerbraten" is a colloid-chemical one. The meat swells in these solutions — the connective tissue more than the muscle — becoming in consequence richer in water, more tender and more digestible. The

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[1] See, for example, the bibliographies in the dissertations of AMHERDT and JUNG from the laboratory of Prof. W. FREI in Zürich.

effects of boiling or roasting meat may also be analyzed colloid-chemically.

§18.

These references to milk, bread and meat do not, of course, exhaust the applications of colloid chemistry to the problem of the preparation of our food stuffs. A colloid-chemical principle is utilized when gelatin is added to ice cream. It serves as a protective colloid for the fine crystals of ice which are formed in the process of freezing, giving these ice crystals a high degree of dispersion and thus the finished product its wished-for body and smoothness.[1]

Colloid-chemical processes are also encountered in the production of mayonnaise[2] and of sauces of various kinds. Adsorption phenomena are called into service when the salt content of a bouillon is decreased so much that the effect may be recognized even by the sense of taste, simply by adding unsalted rice to the bouillon. It is also seen when the good housewife reduces the salt content of a too salty soup by stirring into it an egg. The art of cooking is a colloid-chemical art.

But coffee and tea are also colloid solutions. The former lends itself splendidly to demonstration experiments in diffusion, dialysis, electrophoresis, ultramicroscopy, coagulation, adsorption, etc. Wine and beer, too, are colloid solutions.[3] The colloids of beer are positively charged and their presence gives beer its body and its foaming qualities. A beer problem of a distinctly colloid-chemical nature has proved of interest to Americans. Since they are accustomed to consume their beer at a temperature lying near the freezing point, the beer was found often to become turbid. This is due to the fact

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[1] See J. Alexander, Koll.-Zeitschr., **5**, 101 (1909); **6**, 197 (1910).

[2] See Martin H. Fischer and Marian O. Hooker, Fats and Fatty Degeneration, New York, 1917.

[3] Many original papers or abstracts of the work of F. Emslander, A. Reichardt, H. Lüers, W. Windisch, W. Dietrich, etc., on the colloid chemistry of beer appear in the Kolloid-Zeitschrift.

that the colloid proteins of beer tend to precipitate at these low temperatures. By adding hydrating substances to the beer like lactic acid or traces of proteolytic ferments, it was found possible to hydrate the proteins so heavily that they no longer settled out. This trick must impress every colloid chemist as highly amusing, for to accomplish it the very substances are used which in the body are responsible for the production of edema. The Americans literally consume beer which has been rendered "edematous."

Colloid-chemical principles are utilized in the *refining of sugar*. In this the sugar is separated from its colloid accompaniments by processes of diffusion, dialysis, etc. We are face to face here with technical questions through the solution of which I was told in America fortunes may be made. Various cane sugar molasses containing great quantities of sugar are sold as cattle feed, simply because the sugar cannot be separated from its colloid accompaniments. We seem to deal in these instances with adsorption compounds between pectin-like substances and sugar, and the colloid-chemical problem involved is that of the destruction of this combination.[1]

In the official testing of foodstuffs, colloid-chemical methods are used for the discovery of adulterants. I have already touched upon LEY's silver test for the distinction of natural from artificial honey. A colloid-chemical method for discovering the addition of agar to fruit jellies and marmalades makes use of the influence which such addition has upon the form and the structure of LIESEGANG rings when formed in such jellies.[2] The principles of emulsification and of stabilization of the emulsions are of importance in the manufacture of *oleomargarine*.

Perhaps I have exhausted your patience by this endless recital. But is it my fault that relations are so intimate

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[1] See, for example, the newer studies of PEEK, Intern. Sugar Jour., **21,** 70 (1919) and F. W. ZERBAN, Jour. Ind. Eng. Chem., **12,** 744 (1920).

[2] See the paper of E. MARRIAGE, Koll.-Zeitschr., **11,** 1 (1912).

that every colloid chemist needs to greet every good cook as a colleague?

But wherein lies the progress to be expected of a conscious application of colloid chemistry to food chemistry? We have made butter and cheese and baked bread for ages past without any knowledge of colloid chemistry. Colloid-chemical treatment of these questions brings new terms but does it also bring us new things and not merely a rehash of the old?

It must be admitted that even colloid chemistry can not make caviar of turnips and that it can not be a patent medicine cure for every difficulty of industrial practice. Nevertheless, colloid chemistry does produce practical results. One may buy fresh breakfast rolls in the cities of Holland, for example, in spite of the fact that night baking is forbidden. J. R. Katz has shown how rolls may be baked one day and still be fresh the next. But the colloid chemist would be satisfied without such practical results if he could contribute to a better understanding of what is already known, for *to understand better the nature of what has been done is to know better what may be done.*

Every new science has to produce its new terminology. But when flour is defined as a mixture of three hydrogels of which two (protein and starch, are lyophilic, something more is given than new words. It is made clear that the constituents of flour are capable of swelling and that this swelling is greater for starch and protein than for cellulose. It follows that the laws which colloid chemistry has discovered for the behavior of lyophilic substances hold for the constituents of flour. But whoever makes such a new definition must assume, too, full responsibility for the associated truths, It is serious work therefore when even old and familiar phenomena are redefined[1] colloid-chemically. With this I do not wish to deny that the thing has, at times, been done

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[1] An illustration taken from another field may serve to clarify the situation. It was known even before the theory of electrolytic dissociation was advanced that silver nitrate would react with "dissolved" chlorine compounds. Today we say that silver nitrate is a reagent for "chlorions." No one will deny the

superficially and with little conscience, but if such errors — hardly to be avoided in any rapidly growing science — are overlooked, the fact remains that colloid chemistry is of inestimable theoretical and practical value to the food chemist. That much remains to be done should be occasion for joy. Let us at it.

§19.

Colloid chemistry has something to say about *fuels*. Why has fresh coke a greater (maximal) capacity for holding water than aged coke? It seems to me that this is another case of syneresis. As H. Winter has recently shown[1], coke and hard coal must obviously be the carriers of highly dispersed systems similar to gels when the origin of these substances and their relation to soft coal, lignite, peat, wood, etc., is remembered.

Why does it not pay to squeeze the water from peat by mechanical methods? It is because it is bound to the peat as hydration water and it requires many atmospheres pressure to bring about separation. This is why all rational present day or future methods must start with the separation of this colloidally bound water through the addition of coagulating chemicals, through the destruction of the gels by autoclaving at 180° C. or thereabouts (the Ekeberg process) or through the plentiful use of time, for peat also shows in beautiful fashion the phenomenon of syneresis, that is to say, a spontaneous giving off of its dispersion medium with time. Peat spread out during the summer months dries out greatly in spite of the fact that it is frequently rained upon. In this instance, of course time means money.[2]

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progress represented by such a "restatement of the fact in other words" with all its consequences as now embraced in our concept of the "ion."

[1] H. Winter, Koll.-Zeitschr., **19**, 8 (1916).

[2] Hay also shows syneresis as demonstrated by the fact that it "sweats" after having been dried superficially. For a discussion of this question and its rôle in the spontaneous combustion of hay, etc., see G. Laupper, Landwirtschaftl. Jahrb. d. Schweiz, 1920 (reprint).

When raw fuels, in order to save their valuable by-products, are first subjected to coking or fractional distillation, limitless dispersed systems like suspensions, emulsions and foams are encountered. The production, destruction or conservation of these belongs to the most important as well as most difficult of the problems of these industries.

The mineral oil industry is permeated with colloid problems. As D. HOLDE[1] has shown, crude oil and some of its various fractions contain materials which, like the asphalts, are present in typically colloid subdivision. The fundamental process of dehydrating crude oil represents nothing but the coagulation of a water-in-oil emulsion; and its purification through the addition of solid adsorbents, like Florida earth, or by means of electrophoresis, is nothing but a giant colloid reaction. When liquid fuels are burned in motors, etc., the attempt is made to disperse them as highly as possible through a suitable dispersion apparatus (the carburetor). "Colloid coal" has been much discussed lately. The name is given to dispersions of coal dust in fuel oil, the suspensions produced actually being so fine that the coal particles no longer settle out. It has been suggested that coal dust might in this way be used in DIESEL motors but the subject is too new to be ready for discussion.

§20.

Fuels and raw materials enter a factory; finished articles and *waste products*, like waste liquors, sludges, smoke and dust depart from it. To dispose of smoke and dust the methods of dispersoid chemistry must be employed. A hundred years ago HOHLFELD, teacher of mathematics in the Leipzig Thomas School,[2] suggested that the smoke nuisance might be met through the use of electrophoresis discovered

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[1] D. HOLDE, Koll.-Zeitschr., **3,** 270 (1908).

[2] See in this connection the interesting lecture of V. KOHLSCHÜTTER, Nebel, Rauch und Staub, Bern, 1918.

by Reuss in 1809. This idea, developed in our time through the work of the American, F. Cottrell, is used today to this very end. But not only is dust "destroyed" in such fashion but the same method is used in order to recover in ponderable form valuable materials which might otherwise be lost, as potassium from the dust of cement ovens.

When I tell you finally, that a large part of the refuse materials found in our drainage systems (constituting in city sewers, for example, fifty to sixty per cent of the solids contained in the waters flowing through them) is found here in a colloid state and that colloid-chemical methods must in consequence be used to handle them, you will perhaps be inclined to agree with me when I say that things not only begin in colloid chemistry, but in colloid chemistry they end.

§21.

With this I, too, must conclude not only my remarks upon the technical applications of colloid chemistry but the entire series of my lectures. I shall be satisfied if I have succeeded in making clear to you the freshness of the points of view of colloid chemistry, its wealth, and its inexhaustible possibilities of scientific and practical application. It is these which I think justify us in looking upon colloid chemistry as entitled to independent existence.

In retrospect you will, perhaps, be tempted to ask me the following questions. If it is true that we are dealing with a science so rich in ideas and so pregnant with possibilities of scientific application — I presume too much, perhaps, when I assume that my lectures have given you this impression — if all this is true, why is it that colloid chemistry has not long been known as an independent science? Why is it that this science which deals in such large measure with commonplace and everyday sorts of things has been studied systematically for but a few years?

I think that the answers to these questions are about as follows. Physics has until recently busied itself chiefly with the properties of matter in mass; chemistry, on the other hand, has dealt chiefly with the smallest particles of matter such as atoms and molecules. Relatively speaking, we know much of the properties of large masses and we talk much, also, of the properties of molecules and atoms. It is because of this that we have been led to regard everything about us either from the standpoint of physical theory or from that of molecular or atomic theory. We have entirely overlooked the fact that between matter in mass and matter in molecular form there exists a realm in which a whole world of remarkable phenomena occur, governed neither by the laws controlling the behavior of matter in mass nor yet those which govern materials possessed of molecular dimensions. We did not know that this middle country existed, how large a number of natural phenomena belonged in it, nor how greatly the degree of dispersion determined their behavior. We have only recently come to learn that every structure assumes special properties and a special behavior when its particles are so small that they can no longer be recognized microscopically while they are still too large to be called molecules. Only now has the true significance of this region of the colloid dimensions — THE WORLD OF NEGLECTED DIMENSIONS — become manifest to us.

If some of my explanations have seemed not clear or inadequate, I beg you to consider this not as characteristic of colloid chemistry, but as dependent solely upon my personal shortcomings. A science may attain to fullness; her disciples, never.

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